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THE ACTION OF IODINE ON SOLUTIONS OF STANNOUS CHLORIDE.

BY S. W. YOUNG AND MAXWELL ADAMS.

Received April 22, 1897.

THE action of free iodine on stannous chloride appears to have been first studied by Henry.[1] He states that when iodine is treated with an excess of a concentrated stannous chloride solution, bright red crystals of stannous iodide separate from the solution on cooling, while on concentration of the mother-liquors straw-yellow needles separate out, which consist of a definite compound, stannous chloro-iodide, SnICl or SnI_2. $SnCl_2$. This chloro-iodide was immediately decomposed by water, the crystals turning red, and evidently being converted into stannous iodide, while the stannous chloride went into solution.

If an excess of iodine was used, Henry obtained crystals of stannic iodide, on concentrating the solution. The results of his analyses are not in very good accord with the calculated numbers, which fact he ascribes to the difficulty of the analytical methods. More recently a paper has appeared by V. Thomas[2] concerning the action of dry stannous chloride on a solution of iodine in carbon bisulphide. As the conditions in Thomas' experiments were wholly different from those in ours, his paper need not be further mentioned.

This paper embodies some preliminary results of an attempt to make a more thorough and concise investigation of the reaction. The method of experimentation was as follows: A concentra-

[1] *Phil. Trans.*, *1843*, 363. [2] *Compt. rend.*, **122**, 1539.

ted solution of stannous chloride was prepared by the action of concentrated hydrochloric acid on metallic tin. The action was allowed to continue until the evolution of hydrogen became very inconsiderable. This was after about six weeks. During this reaction the solution was protected from the air by a layer of coal oil. It was then rapidly filtered through absorbent cotton and under oil, and kept in this way. The strength of this solution (still containing considerable free hydrochloric acid) was determined as follows:

Ten cc. were diluted to 200 cc. with well boiled water, and twenty cc. portions titrated with standard permanganate solution after the addition of about twenty-five cc. of a one to ten solution of manganese sulphate to guard against the escape of chlorine. The titrations gave closely agreeing results, and the solution was found to contain 0.6818 gram of stannous chloride per cubic centimeter.

Samples for investigation were then prepared by the following method: Ten gram portions of iodine were placed in beakers, and treated with measured volumes of the above solution of stannous chloride, the volumes differing in different samples. The pasty orange-colored mass thus formed was stirred with the addition of small amounts of water from time to time, until the reaction was complete, as indicated by the solution and decolorizing of all the iodine. (No samples containing excess of iodine were prepared.) The action being complete, the beakers and contents were heated on an asbestos plate to boiling, and hot boiled water added until the orange crystalline mass just dissolved. The solutions, on cooling, deposited in most cases needle-shaped crystals, which were rapidly filtered off by suction, dried to some extent quickly with bibulous paper, and finally completely dried *in vacuo* over sulphuric acid. The samples were then carefully powdered and preserved for analysis. All were more or less hygroscopic and some even deliquescent. On long exposure to sunlight the samples experienced some change of color, probably due to oxidation.

DESCRIPTION OF SAMPLES.

Samples OO-A and OO-B.—In the preparation of all samples, except where otherwise stated, ten grams of iodine were used. In

the preparation of samples OO-A and OO-B, and also of sample O, a solution of stannous chloride containing 0.6902 gram of stannous chloride per cubic centimeter was used. In all others the solution mentioned above and containing 0.6818 gram per cubic centimeter was used. Samples OO_A and OO_B were prepared each from ten grams of iodine and 10.6 cc. of stannous chloride, which was just sufficient to decolorize all of the iodine.

Sample OO-A.—Water was added to the sample while hot until the mass of salts dissolved. On cooling, the solution did not deposit any crystals. On standing the solution became dark-colored, owing to iodine being set free from oxidation.

Sample OO-B was prepared in exactly the same way, except that the water was not added to dissolve the orange-colored mass, but instead, this was immediately filtered off, washed slightly with water, and analyzed. The analysis gave:

	Calculated for SnI_4.	Found. I.	II.
I	81.00	79.45	79.43
Cl	....	1.23	1.24
Sn	19.00	19.68	19.64
	100.00	100.36	100.31

On crystallization from glacial acetic acid or carbon bisulphide, the substance gave theoretical numbers for stannic iodide.

In the preparation of these two samples there were present two atoms of iodine for each molecule of stannous chloride. As was to be expected, the reaction is as follows:

$$2SnCl_2 + 4I = SnCl_4 + SnI_4.$$

Sample O.—Ten grams of iodine and twelve cc. stannous chloride. In this preparation there was present a small excess of stannous chloride above that called for in the above equation. Water was added until the product all dissolved on boiling. On cooling the solution deposited a very small quantity of small crystals, which, under the microscope, were seen to be aggregations of needles. Enough for analysis was not obtained. There can be no doubt, however, in the light of the results which follow that these needles were stannous iodide, more or less contaminated with stannous chloride.

Sample I.—Ten grams iodine and 14.1 cc. stannous chloride.

On cooling, the solution deposited a considerable quantity of fern-like masses of light orange crystals, which under the microscope were seen to be aggregates of very small needles.

ANALYSIS.

I	63.26	63.37
Cl	2.60	2.30

The percentage of iodine in pure stannous iodide is 68.05. This product appears to be somewhat impure stannous iodide.

Sample II.—Ten grams iodine and 17.9 cc. stannous chloride. On cooling, fine needles similar to sample I were deposited.

ANALYSIS.

I	63.48	63.46
Cl	2.47	2.52

Sample III.—Ten grams iodine and twenty-two cc. stannous chloride. Needles similar to I and II, but larger and redder.

ANALYSIS.

I	65.13	64.99
Cl	1.65	1.98

Sample IV.—Ten grams iodine and twenty-six cc. stannous chloride. Needles bright red and larger than in III.

ANALYSIS.

I	....	65.12	64.93	65.04
Cl	1.90	1.80	2.08	2.03

Sample V.—Ten grams iodine and thirty cc. stannous chloride. Crystals like IV.

ANALYSIS.

I	65.10	64.91
Cl	2.04	2.09

Sample VI.—Ten grams iodine and thirty-four cc. stannous chloride. Crystals like IV.

ANALYSIS.

I	62.08	62.00
Cl	3.60	3.63

Sample VII.—Ten grams iodine and thirty-eight cc. stannous chloride. Crystals like IV.

ANALYSIS.

I	63.12	63.18
Cl	....	2.59

Sample VIII.—Ten grams iodine and forty-two cc. stannous chloride. Crystals at first formed appeared to be very similar to those of the preceding preparations. However, after the solution had been allowed to stand for a few hours a curious phenomenon was noticed. A number of very light yellow, almost white, patches appeared in various parts of the mass of red crystals. On close examination these patches were seen to be bunches of radiating needles. These gradually spread until they formed a very considerable portion of the whole. As it was impracticable to separate these crystals from the red ones the following method was used to determine what was the difference between the two sorts of crystals. The preparation was repeated, but in double quantity. After bringing all into solution at the boiling-point, the solution was divided into two approximately equal parts. One (VIII-A) was filtered off as soon as the red crystals had formed, and before the white bunches appeared. The other (VIII-B) was allowed to stand for about twenty-four hours. At this time the white patches had appeared in very considerable quantities. The sample was then filtered off and the crystals thoroughly mixed. Analysis would show whether the red and yellow crystals had the same or different composition.

SAMPLE VIII-A. ANALYSIS.

I	59.02	59.00	59.03	59.17
Cl	....	5.01	....	4.96

SAMPLE VIII-B. ANALYSIS.

I	43.40	43.55
Cl	12.79	12.75

Sample IX-A and IX-B.—Twenty grams iodine and ninety-two cc. stannous chloride, divided into two parts, as in the preceding. In IX-B, before filtering the light yellow crystals had almost wholly replaced the red ones.

SAMPLE IX-A. ANALYSIS.

I	61.63	61.76
Cl	3.34	3.45

SAMPLE IX-B. ANALYSIS.

I	42.60	42.70
Cl	14.20	14.35

Samples X-A and X-B.—Twenty grams iodine and 100 cc. stannous chloride divided into two portions.

Products similar to preceding, except that yellow patches appeared before the solutions were wholly cool. Sample X-A was therefore filtered while still somewhat warm. Sample X-B was almost wholly changed over into the light yellow crystals.

SAMPLE X-A. ANALYSIS.

I	56.10	56.14	56.05
Cl	6.92	6.99	6.95

SAMPLE X-B. ANALYSIS.

I	40.09	39.83	39.99	39.80
Cl	....	16.03	....	15.81

Samples XI-A and XI-B.—19.14 grams iodine and 103.4 cc. stannous chloride. Analogous to preceding, but still greater precaution was necessary to prevent XI-A from becoming converted into the yellow substance before it could be filtered. XI-B was practically all yellow before filtering.

SAMPLE XI-A. ANALYSIS.

I	58.59	58.56
Cl	5.77	5.97

SAMPLE XI-B. ANALYSIS.

I	39.57	39.51
Cl	15.64	15.64

Following is a tabulated statement of the above results, together with certain derived calculations. In the first column is placed the number of grams of iodine used in the preparation of the sample. In the second column are the weights of stannous chloride used. These are calculated by means of the standard of the solution. In the third column (headed R) are the ratios of the numbers of atoms of iodine used to the number of molecules of stannous chloride. Thus the number 1.21 after Sample II means that in the preparation of that sample there were used for each molecule of stannous chloride, 1.21 atoms of iodine. The fourth and fifth columns contain the analytical data, averages being used. Columns six and seven contain the percentages of stannous iodide and of stannous chloride calculated from the percentages of iodine and chlorine. These results add up

sufficiently close to 100 per cent., when it is considered that errors have been very considerably magnified by the processes of calculation.

TABLE.

No. of sample.	I. Grams.	$SnCl_2$. Grams.	R.	Iodine. Per cent.	Chlorine. Per cent.	SnI_2. Per cent.	$SnCl_2$. Per cent.	R'.
OO-A	10	7.32	2.000	....	....	....	....	....
OO-B	10	7.32	2.000	79.44	1.24	....	....	....
O	10	8.28	1.770	....	....	....	....	....
I.....	10	9.61	1.540	63.31	2.65	92.60	7.08	14.90
II.....	10	12.20	1.210	63.47	2.50	92.83	6.69	14.30
III.....	10	15.00	0.984	65.06	1.81	95.15	4.85	10.08
IV	10	17.72	0.832	65.03	1.95	95.10	5.22	10.87
V	10	20.45	0.723	65.00	2.06	95.06	5.51	11.50
VI	10	23.18	0.637	62.04	3.61	90.74	9.67	21.11
VII	10	25.91	0.570	63.15	2.59	92.34	6.94	14.85
VIII-A...	10	28.63	0.515	59.05	4.98	86.58	13.34	30.59
VIII-B ...	10	28.63	0.515	43.47	12.77	63.57	34.20	106.50
IX-A.....	10	31.37	0.470	61.70	3.40	90.24	9.11	19.99
IX-B.....	10	31.37	0.470	42.70	14.27	62.44	38.20	121.30
X-A.....	10	34.09	0.433	56.10	6.95	82.06	18.61	44.93
X-B.....	10	34.09	0.433	39.96	15.92	58.45	42.65	144.50
XI-A.....	9.57	35.25	0.403	58.58	5.87	85.69	15.71	36.34
XI-B.....	9.57	35.25	0.403	39.18	15.64	57.31	41.88	145.00

DISCUSSION OF RESULTS.

It will be noticed that samples I to VII inclusive consist of stannous iodide mixed with small and somewhat variable amounts of stannous chloride. As has been previously stated, the first action of iodine on stannous chloride is to be expressed by the following equation :

$$(1)\quad 2SnCl_2 + 4I = SnCl_4 + SnI_4.$$

The second step, which occurs when excess of stannous chloride is added, is the reduction of the stannic iodide to stannous iodide by the stannous chloride, according to the equation :

$$(2)\quad SnI_4 + 2SnCl_2 = 2SnI_2 + SnCl_4.$$

That this reaction is not a complete one appears likely from the fact that even in sample I, where only a very slight excess of stannous chloride over the amount called for in equation (1) is present, this excess is not wholly oxidized, since the crystals which deposit from such a solution contain a very noticeable proportion of stannous chloride (seven per cent.). In sample

III, R is almost exactly unity, and the equation representing the condition at this point is:

$$2SnCl_2 + 2I = SnI_2 + SnCl_4.$$

That is, if the reaction were complete at this point all of the stannic iodide would have just been reduced to stannous iodide. Since all of the crystals obtained in these preparations contain stannous chloride in significant quantities, it appears, as is suggested above, that the reaction is not complete, but that rather an equilibrium occurs in which stannous and stannic chlorides and stannous and stannic iodides exist side by side. An investigation upon this point is being attempted.

All samples from I to VII, inclusive, show small but significant amounts of stannous chloride (from five to ten per cent.). Samples VIII-A to XI-A (excluding B samples) contain somewhat larger but still variable amounts of stannous chloride. Samples VIII-A and VIII-B differ very markedly from one another, and the same is true of all other A and B pairs. The B samples always contain a much larger amount of stannous chloride than the A samples. It thus appears that the transformation of the red needles into the yellow is accompanied by a very distinct change in composition. Analyses of the yellow needles (B samples) show that they vary considerably in composition (from thirty-four to forty-two per cent. of stannous chloride). Thus the yellow needles are not only different from the red, but they show no constancy of composition among themselves.

Following are the results of some analyses of these yellow bodies (which vary in color from deep yellow to nearly white) which were prepared during some preliminary work on this subject, by using varying excesses of stannous chloride, unfortunately, however, not measured. The excess increased, however, from A to D.

	A.		B.	
	I.	II.	I.	II.
I.....	42.27	42.25	23.26	23.33
Cl.....	13.96	14.08	29.01	28.98

	C.		D.	
	I.	II.	I.	II.
I.....	8.47	8.55	1.73	1.81
Cl.....	...	. .	...	...

These results show that by using sufficient excess of stannous

chloride it is possible to obtain crystals that are very low in stannous iodide. It will also be noticed from the results given in the table that the amounts of stannous chloride crystallizing out with the stannous iodide after standing (*i. e.*, in B samples), are roughly proportional to the excesses of stannous chloride used.

These facts led immediately to the conclusion that all these crystalline substances are isomorphic mixtures of stannous chloride and iodide, and that these two salts can form crystals containing the two salts in any proportion. It seems pretty certain that Henry's so-called compound SnICl was no true compound, but merely an isomorphic mixture in nearly equivalent proportions, whose occurrence was purely accidental.

The fact that from all the preparations described in the table, the first crystals to form were red, and shown to consist very largely of stannous iodide, while the yellow crystals in those cases in which they formed at all, only came later, and formed slowly and at the expense of the red crystals is due undoubtedly to differences in equilibrium in the solutions at high and at low temperatures. The conditions are such at high temperatures that approximately pure stannous iodide separates. At lower temperatures, providing sufficient stannous chloride is present, the conditions of solubility are such that crystals containing larger amounts of stannous chloride form, while the stannous iodide first formed is slowly redissolved. It appears probable that crystallization from saturated solutions containing both salts presents a somewhat complicated problem in equilibrium, the equilibrium depending upon the relative amounts of the two salts present and upon the temperature as influencing their mutual solubilities.

Aside from facts already discussed there are two others which seem to indicate that such is the case. In the first place, on warming the yellow crystals in their mother-liquor, they turn red. Evidently this is due to the more rapid solution of stannous chloride with increasing temperature. The same result may frequently be attained by treating the yellow crystals with pure water or with a little dilute hydrochloric acid.

In the second place, when a solution of the mixed salts in such proportions that yellow needles will deposit from the beginning (red needles do not form if sufficient excess of stannous

chloride is used) is allowed to deposit by slow cooling, the crystals at the bottom (*i. e.*, those first deposited) are higher in iodine than those on the top. Two such solutions were prepared and allowed to stand. After all crystals had deposited the top portions were dipped out, dried, and analyzed. The same was done with the bottom portions. Following are the results of the analyses :

	A.		B.	
	Top.		Top.	
	I.	II.	I.	II.
I.....	40.19	40.00	40.01	40.19
	Bottom.		Bottom.	
I.....	43.20	43.38	40.90	41.00

Investigations are now under way in this laboratory, with the object of throwing some clearer light upon these points.

ANALYTICAL METHODS AND NOTES.

1. *Determination of Tin.*—This was determined in only a few cases, it being found preferable to determine iodine and chlorine, than iodine and tin. When tin was determined the method of precipitation as metastannic acid was used, except in a few cases, where but very little chlorine was present. In these cases the weighed sample was treated in a porcelain crucible with two or three cc. of concentrated nitric acid, evaporated to dryness on the water-bath, the residue ignited and weighed as stannic oxide. Total analyses usually fell a little short of 100 per cent. This was undoubtedly due to slight oxidation having taken place in the drying of the samples.

2. *Determination of Iodine and Chlorine.*—Instead of using ferric chloride, as is customary, to set free the iodine, ferric sulphate was used. The iodine was distilled off as usual in the Bunsen apparatus, and titrated with thiosulphate. To the residual liquid (which still contained all the chlorine) ten cc. of a strong solution of potassium permanganate was added, and the distillation was continued into a separate receiver containing potassium iodide solution. The iodine thus set free was titrated with thiosulphate as in the iodine determination. Care is necessary at the beginning of this distillation to prevent some of the solution from being carried over mechanically. The method gives good results, but requires careful manipulation. Hart[1] has already suggested the use of the method qualitatively, and

[1] *Ztschr. anal. Chem.*, **24**, 182.

it is likely that White[1] describes the quantitative application of it in much the same form as is given above. The original paper not being at hand this is not positively known.

STANFORD UNIVERSITY, April 15, 1897.

THE AMOUNT AND PROPERTIES OF THE PROTEIDS OF THE MAIZE KERNEL.[2]

BY THOMAS B. OSBORNE.

Received April 12, 1897.

SOME time since Prof. R. H. Chittenden and the writer published the results of an extended investigation of the proteids of this seed.[3] In that paper no definite statements were made respecting the quantities of the various proteids found, nor were the properties of some of them as fully described as is now possible. For these reasons the results of some additional researches are here put on record.

The proteids of the maize kernel may be distinguished according to their solubilities as follows:

a. Proteid, soluble in pure water, having some of the properties of proteose.

b. Globulins, insoluble in pure water, but soluble in salt solutions.

c. Proteid, insoluble in water and salt solutions, but soluble in alcohol of sixty to ninety-nine per cent.

d. Proteid matter, insoluble in water, salt solutions and alcohol, but soluble in dilute alkalies and acids.

a. PROTEID SOLUBLE IN WATER.

If the substance precipitated from an aqueous extract of yellow corn meal by saturating with ammonium sulphate, is dissolved in water and the resulting solution dialyzed, the globulins extracted from the meal by aid of the soluble mineral constituents of the seed are *largely* precipitated. If these globulins are next *completely* removed by heating the solution to 80° and the filtrate therefrom be precipitated by an excess of alcohol, a small quantity of proteid is obtained having many of the reactions characteristic of proteose. A recent determination showed

[1] *Chem. News*, 58,229.

[2] From the Report of the Connecticut Agricultural Experiment Station for 1896.

[3] *Am. Chem. J.*, 13, 453, 529, and 14, 20. Abstract in Report of Conn. Agr. Expt. Station for 1891, p. 136.

the presence of only 0.06 per cent. of this body. The quantity found was too small for a satisfactory study of the properties of the substance, but the following observations were made. Dissolved in a little water, only a very small quantity of undissolved substance remained, showing the nearly complete removal of proteid coagulable by alcohol. The clear filtrate from this insoluble matter when diluted with an equal volume of distilled *water* gave a considerable coagulum on boiling, but when diluted with the same quantity of *ten per cent. salt solution* only an opalescence resulted on boiling. Nitric acid added to the aqueous solution gave a heavy precipitate which nearly all dissolved on warming, with the production of a strong yellow color, and reappeared on cooling. Saturation of its solution with sodium chloride gave a precipitate much increased by the addition of acetic acid, the filtrate from which was not further precipitated on adding nitric acid. The biuret reaction was violet, not rose red, as is usually given by proteoses. This color reaction, however, was probably modified by the color substance associated with the proteid. Sulphate of copper gave with solutions of this proteose only a turbidity. These reactions do not altogether agree with those given by the proteoses which result from the action of enzymes on native proteids. It is possible that future investigation will show that the so-called proteoses found in seeds belong to a different order of proteids from those usually formed by proteolysis.

In the paper already referred to, a substance is described as albumin which was obtained from solutions that were supposed to have been freed from globulin by prolonged dialysis, by adding thereto ten per cent. of sodium chloride and precipitating with very dilute hydrochloric acid. My recent experience in investigating plant proteids has shown that it is extremely difficult and in many cases impossible to completely precipitate all of the very soluble globulins by dialysis, and since the composition of the so-called albumin thus obtained agreed quite closely with that of a very soluble globulin separated from these solutions by prolonged dialysis, and also since the globulin and the so-called albumin coagulated at about the same temperature, I now feel convinced that the two substances are identical, the latter being a part of the globulin which was not precipitated by

dialysis. In the former paper attention was called to the fact that this body, in some respects, resembled a globulin more closely than an albumin.

In the former paper were also described, as albumin, coagula obtained by concentrating solutions supposed to have been freed from globulin by dialysis and heating to 100°. It was there suggested that these coagula were probably alteration products of the proteids in solution. Since then "proteoses" from many different seeds have been found to yield coagula under similar conditions. It seems therefore quite certain that no true albumin exists in maize kernel.

b. PROTEIDS SOLUBLE IN SALINE SOLUTIONS.

If an aqueous extract of yellow corn meal is dialyzed for some time, a proteid, having the properties of a globulin, is precipitated which was found to have the following composition:

MAYSIN.

Carbon	52.68
Hydrogen	7.02
Nitrogen	16.76
Sulphur	1.30
Oxygen	22.24
	100.00

In our paper on the proteids of this seed, Prof. Chittenden and myself designated this globulin "maize myosin." Further study of plant proteids has shown that no sharp distinction can be drawn between plant myosin and plant vitellin, and I now propose to call this proteid *maysin*, in reference to the specific botanical name *mays*. This globulin readily loses its solubility in saline solutions after precipitation, and therefore the amount present in the seed was underestimated in our former paper. A recent determination in yellow corn meal gave 0.25 per cent.

This proteid is readily soluble in very dilute saline solutions so that it is completely extracted from corn meal by water. Dissolved in ten per cent. sodium chloride brine it is coagulated by heating to 70°.

After separating maysin from the extract of corn meal by dialysis, further prolonged dialysis throws down a small quantity of another globulin having the following composition:

MAIZE GLOBULIN.

Carbon	52.38
Hydrogen	6.82
Nitrogen	15.25
Sulphur	1.26
Oxygen	24.29
	100.00

This is the globulin which seems to be identical with the "albumin" which was formerly obtained by precipitation with salt and acid. This proteid was found in very small amount, twenty-five kilos of fine meal yielding only four and one-tenth grams by dialysis and three and four-tenths grams by precipitation with salt and acid, that is, seven and five-tenths grams in all or 0.03 per cent. of the meal. This figure cannot be taken as representing quite accurately the total quantity present, for doubtless some was lost in consequence of the globulin becoming insoluble and some also through incomplete extraction. The total quantity, however, is exceedingly small, probably not more than 0.04 per cent.

Dissolved in ten per cent. sodium chloride solution, this globulin coagulates on heating to 62°.

If yellow corn meal, after thorough extraction with water, is treated with ten per cent. salt solution, a further quantity of globulin is extracted, which is readily precipitated by dialysis in well developed spheroids.

This globulin, formerly designated maize vitellin, agrees in composition and reactions and is, doubtless, identical with edestin which I have found in various seeds.

A recent determination of edestin in the seed of yellow corn showed the presence of but 0.06 per cent. The quantities obtained in the former investigations were 0.06, 0.10 and 0.10 per cent. The composition of this globulin is as follows:

MAIZE EDESTIN.

Carbon	51.43
Hydrogen	6.86
Nitrogen	18.06
Sulphur	0.86
Oxygen	22.79
	100.00

Edestin is much less soluble in saline solutions than the two globulins previously described, and for this reason is readily precipitated by dialysis or dilution. In warm dilute salt solutions it dissolves freely, but on cooling, separates more or less completely, according to the temperature and the strength of the salt solution. Dissolved in ten per cent. sodium chloride brine, it is partly coagulated by heating above 90°, but even on boiling the coagulation is far from complete.

c. PROTEID SOLUBLE IN DILUTE ALCOHOL.

Finely ground maize meal when extracted by hot alcohol loses eight-tenths per cent. of nitrogen, equivalent to five per cent. of the characteristic proteid called maize-fibrin by Ritthausen, but first described by Prof. Gorham, of Harvard University, in 1821, and named by him zein. The composition of zein, as shown by the average of nine closely agreeing analyses of as many preparations, is the following:

ZEIN.

Carbon	55.23
Hydrogen	7.26
Nitrogen	16.13
Sulphur	0.60
Oxygen	20.78
	100.00

Zein is in many ways a remarkable proteid. It dissolves abundantly in ethyl alcohol of 0.820 specific gravity, forming solutions which, on evaporation in thin layers, leave a perfectly transparent sheet of the proteid.

In *absolute* alcohol, as also in water, zein is wholly insoluble, but in mixtures of water and alcohol it dissolves to a greater or less extent, according to the proportions of the two liquids. It is most soluble in alcohol of from eighty-five to ninety-five per cent., and dissolves but little in alcohol of less than fifty per cent. Solutions of zein in diluted alcohol deposit the proteid on evaporation as the proportion of water in the solution increases. Strong alcoholic solutions of zein gradually coagulate to transparent jellies, which, on long standing, become hard and solid. In ninety-five per cent. methyl alcohol and in commercial propyl alcohol hydrate, zein dissolves readily.

In concentrated glycerol, zein is freely soluble on heating to

about 150° C., to solutions which, when much is dissolved, solidify on cooling to 20°. In such solutions zein can be heated to 200° C. without undergoing any apparent change, for, on pouring them into water, the zein separates as a pulverulent precipitate readily and completely soluble in dilute alcohol.

In crystallized phenol, zein is readily soluble on warming, yielding solutions which leave on evaporation clear films of unchanged zein. In glacial acetic acid, zein dissolves in large proportion and is left, by evaporating the acid on a boiling water-bath, in transparent films of apparently unchanged proteid, which readily dissolve in alcohol.

Strong solutions of zein in glacial acetic acid when poured rapidly into water give large coherent precipitates which retain all the original properties of the proteid; if the solution is dilute the zein is, to a greater or less extent, dissolved by the aqueous acetic acid.

In one-half per cent. sodium carbonate solution and in two-tenths per cent. hydrochloric acid, zein is wholly insoluble even when warmed for twenty-four hours at 40°.

In one-tenth to two per cent. caustic potash solution, zein is very readily dissolved and even by heating to 40° for twenty-four hours in such solutions is not converted into "alkali-albumin," for the precipitate obtained by neutralizing solutions so treated is completely soluble in alcohol.

Alcoholic solutions of zein are not precipitated by tannin, picric acid, trichloracetic acid, lead acetate, silver nitrate, mercuric chloride, ferric chloride, or potassio-mercuric iodide. Clear solutions mixed with silver nitrate dissolved in alcohol leave clear films when evaporated on glass, which gradually turn deep red on exposure to sunlight. When hydrochloric acid in considerable quantity is added to a solution of zein in ethyl alcohol containing much silver nitrate, no precipitate is produced until the mixture has stood for some time, when a turbidity gradually develops which is affected but slowly by light. If the mixture of acid, zein and silver nitrate is boiled it becomes turbid at once.

Zein treated with an alcoholic solution of ferric chloride shows no visible change, but if tested with potassium ferricyanide a deep blue solution is formed, showing that the ferric chloride is reduced at once.

Potassium ferricyanide added to the zein solution is not reduced even after standing some hours.

On digestion with pepsin in hydrochloric acid, zein is converted into proteoses and peptones.[1]

According to J. G. C. T. Kjeldahl (*Bied. Centr., 1896*, **25**, 197, from Forhandl. Skand. Naturfors, *1892*, 385–390) zein dissolved in seventy-five per cent. alcohol has a specific rotation of $(\alpha)_D$—35° and in glacial acetic acid $(\alpha)_D$—28°.

d. PROTEID MATTER SOLUBLE IN ALKALIES.

This was estimated as follows : One hundred grams of very finely ground maize meal which contained 1.54 grams of nitrogen were successively exhausted with two-tenths per cent. potash water and with alcohol. The dried residue weighed seventy-seven grams and contained 0.1645 gram of nitrogen. Accordingly, 1.3755 grams of nitrogen, including that of all the soluble proteids, had been extracted. This amount multiplied by the factor 6.25 gives the total quantity of soluble proteids, *viz.*, 8.5969 grams. Subtracting therefrom the sum of the several proteids previously determined, *viz.*, zein five grams, globulins 0.39 gram and proteose 0.06 gram, there remains 3.1469 grams of proteid insoluble in salt solutions and alcohol, but soluble in dilute potash water.

The alkaline extract obtained in estimating the quantity of this proteid was filtered perfectly clear, neutralized with acetic acid, the precipitate filtered out, washed thoroughly with water and extracted with hot alcohol to remove zein.

The proteid residue was then redissolved in dilute potash water, filtered clear and again precipitated by neutralization with acetic acid and thoroughly washed with water, with hot alcohol, and finally with ether. After drying at 110° the preparation was analyzed with the following results :

Carbon	51.26
Hydrogen	6.72
Nitrogen	15.82
Sulphur	0.90
Oxygen	25.30
	100.00
Ash	2.38

[1] Chittenden : *Medical Record*, 45, 487.

The results of this analysis do not indicate that this substance has any relation to the other proteids already described. Owing to its insolubility in neutral fluids no characteristic reactions could be obtained, and accordingly nothing more was learned respecting it.

The foregoing statements show that 100 grams of the yellow corn meal contained approximately:

Proteid soluble in two-tenths per cent. potash....	3.15	grams	containing	15.82	per cent.	N.	= 0.4983	gms.
Zein	5.00	"	"	16.13	"	"	= 0.8065	"
Very soluble globulin	0.04	"	"	15.25	"	"	= 0.0061	"
Edestin	0.10	"	"	18.10	"	"	= 0.0181	"
Maysin	0.25	"	"	16.70	"	"	= 0.0417	"
Proteose	0.06	"	"	17.00	"	"	= 0.0102	"
							1.3809	"
Nitrogen undissolved by dilute potash water							0.1645	"
Total							1.5454	"
Nitrogen in meal by analysis.....							1.5400	"
Mean percentage of nitrogen in Maize Proteids							16.057	

THE COMMERCIAL PREPARATION OF NITRONAPHTHALENES.

By William H. Krug and J. E. Blomén.

Received May 15, 1897.

THE manufacture of nitronaphthalenes has of recent years acquired considerable importance in the arts, and particularly in the explosive industry. In this industry it has been utilized in various ways and for different purposes. The late Nobel was the first to point out that the addition of nitronaphthalene to a nitroglycerol explosive, such as nitrogelatin, rendered this practically non-sensitive to concussion, and this property has been and is still widely applied to render the handling of nitroglycerol explosives more safe.

In the manufacture of nitro substitution powders, nitronaphthalene soon replaced the more expensive nitrobenzol as a basis, and a large number of patents were taken out for its use with oxidizing agents alone or with an admixture of sensitizing agents, such as nitroglycerol, picric acid, etc. A third use was found for nitronaphthalene when it was discovered that it seemingly ren-

dered dynamite "non-freezable." Even a small admixture of nitronaphthalene causes dynamite to remain soft to the touch at low temperatures, and it has therefore been extensively used for the manufacture of non-freezing dynamite. It has been proved that this advantage is only chimerical; the addition of nitronaphthalene in no wise changes the properties which are characteristic of nitroglycerol at low temperatures, but in fact adds a new element of danger, as it makes it impossible for the miner to determine whether the dynamite should be thawed before use.

Still another use of nitronaphthalene was taken advantage of in its property of rendering dynamite "fumeless," but this has not yet been definitely proved. In the manufacture of plastic dynamites it has always been difficult to obtain a nitrocellulose which gelatinizes perfectly in the nitroglycerol. An addition of nitronaphthalene will considerably increase the solvent action of nitroglycerol on nitrocellulose, *i. e.*, even higher nitration degrees than trinitrocellulose may be dissolved when nitronaphthalene is added to the nitroglycerol. The vast importance of this property will be realized by any manufacturer who has a large quantity of the expensive nitrocellulose rejected on account of its insolubility in nitroglycerol.

Almost every manufacturer of explosives has been confronted with the problem of preparing nitronaphthalene in a practical and economical way, but has found that very little of practical value has been published on this important subject.

In speaking of nitronaphthalene, a mixture of the nitronaphthalenes is always meant. When the nitronaphthalene is used in conjunction with nitroglycerol its melting-point is of minor importance, but it is desirable to have as high a degree of nitration as possible, since this will retard the momentum of the explosion to a less degree. When used with other sensitizing agents, such as picric acid, it is obvious that the melting-point must be below the decomposition-point of this agent. When it is desired to use a higher nitronaphthalene in this connection it may be accomplished by adding a small amount of mononitronaphthalene, as the latter acts as a solvent of the higher nitro derivatives, and they together will dissolve picric acid, nitrocellulose and the like.

The investigations, which form the basis of this paper, were

undertaken to determine under what conditions the largest yield of suitable nitronaphthalenes could be obtained. The nitro derivatives of naphthalene are generally obtained either by the action of nitric acid alone or mixtures of nitric and sulphuric acids on naphthalene, or for the highest nitro derivatives by renitration of the lower nitronaphthalenes. It has been suggested at different times to prepare the higher derivatives by the nitration of naphthalene-sulphonic acid similarly to the preparation of nitrophenols from phenolsulphonic acid. To ascertain the practicability of this proposition the following experiments were made:

α-Naphthalene-sulphonic acid was prepared by heating naphthalene to 100° C. for about eight hours with one, two, and three times the amount of sulphuric acid required by theory. A fourth preparation was made, using a large excess of sulphuric acid. This last preparation was the only one which appeared free from naphthalene, the substitution being practically complete. It had no odor, was free from naphthalene crystals and gave a clear solution with water.

A quantity of each of these preparations corresponding to ten grams naphtalin, was weighed into flasks and treated in one series with forty grams 36° B. nitric acid, and in another series with thirty grams of the same acid. This strength acid was chosen because it most nearly represents the waste acid recovered in the regaining works of nitroglycerol plants. The stronger acid, 1.42 sp. gr., is so much more expensive that its use is practically out of the question in the commercial preparation of nitronaphthalenes. The action is furthermore so violent when it is used that there is considerable loss of naphthalene through sublimation, and the gain in yield is not proportionally higher. Dilution below 36° B. offers no advantages, as we will show, and is therefore not necessary.

The nitrations were made on a water-bath and were considered complete some time after the red fumes ceased to come off. The resulting mass was melted under water and washed in this state until acid-free. It was then carefully dried on watch-glasses and weighed. When the nitronaphthalenes are used with nitroglycerol or nitrocellulose, it is very important that it should be neutral, and it may even be slightly alkaline. We have

found that this cannot be done with a weak solution of alkali, as it decomposes the product, giving a deep yellow solution. It may, however, be done with a weak solution of sodium carbonate.

The results were :

SERIES I.—FORTY GRAMS 36° B. NITRIC ACID.

No.	Weight of product.	Color.	Odor.	Melting-point.	Remarks.
1	13.3661	yellow	strong	49.0°	crystalline mass, soft
1A	12.8342	"	"	50.0°	" " "
Mean	13.1002				
2	7.6504	yellow	strong	50.0°	crystalline mass, soft
2A	7.0289	"	"	52.0°	" " "
Mean	7.3397				
3	1.0022	greyish-yellow	slight	152.0°	fine silky crystals
3A	0.8288	yellow	"	....	" " "
Mean	0.9155				
4	0.0514	brown-yellow	none	....	solid crystalline mass
5	0.4830	pale yellow	none	150.0°	fine crystals
5A	1.3017	" "	"	....	" "
Mean	0.8923				

SERIES II.—THIRTY GRAMS 36° B. ACID.

No.	Weight of product.	Color.	Odor.	Melting-point.	Remarks.
1	10.6374	orange	strong	54.0°	crystalline mass, soft
2	9.6721	yellow	strong	57.0°	crystalline mass, soft
2A	13.6125	orange-yellow	"	52.0°	" " "
Mean	11.6423				
3	0.7623	greyish-yellow	slight	163.0°	bulky fine crystals
3A	0.4714	yellow	"	....	" " "
Mean	0.6169				
4	0.0227	brown	none	....	slightly crystalline mass
5	0.8708	almost white	none	165.0°	crystals
5A	0.3020	pale yellow	"	....	"
Mean	0.5864				

No. 1. Pure naphthalene.

No. 2. Naphthalene treated with the theoretical amount of sulphuric acid.

No. 3. Naphthalene treated with twice the theoretical amount of sulphuric acid.

No. 4. Naphthalene treated with three times the theoretical amount of sulphuric acid.

No. 5. Naphthalene treated with excess sulphuric acid.

It will be seen that the two series correspond quite closely

in every respect, and that the yield decreases proportionately with the extent of sulphonation. It is therefore impossible under these conditions to prepare nitronaphthalenes from α-naphthalene-sulphonic acid although a higher nitration degree is obtained than with pure naphthalene. The products obtained with the latter seem to be practically mononitronaphthalene, and previous sulphonation in the other tests was so incomplete that the advantage to be gained by it is not apparent.

We next turned our attention to the preparation of the nitronaphthalenes from naphthalene direct with a view of determining the mixture of nitric and sulphuric acids which would give the best results. Ten grams of naphthalene were used in each experiment. The sulphuric acid was mixed with the nitric acid before adding it to the naphthalene and the amount used corresponded to that present in the tests of the first series.

SET 1.—30.23 GRAMS NITRIC ACID USED CORRESPONDING TO FORTY GRAMS 36° B. ACID.

No.	Weight H_2SO_4.	Weight of product.	Color.	Odor.	Melting-point.	Remarks.
1	8.0	14.3470	orange	strong	86.0°	crystalline mass, soft
1A	8.0	14.2646	"	"	99.0°	" " "
		Mean 14.3058				
2	16.0	14.5964	orange	strong	116.0°	crystalline mass, hard
2A	16.0	14.6278	"	"	124.0°	" " "
		Mean 14.6121				
3	24.0	15.2593	yellow	none	136.0°	no visible crystals, hard
3A	24.0	14.8473	"	"	139.0°	" " " "
		Mean 15.0533				
4	52.4	16.9195	light yellow	none	112.5°	no visible crystals, hard
4A	52.4	17.2489	"	"	109.0°	" " " "
		Mean 17.0847				

SET 2.—22.67 GRAMS NITRIC ACID USED CORRESPONDING TO THIRTY GRAMS 36° B. ACID.

No.	Weight H_2SO_4.	Weight of product.	Color.	Odor.	Melting-point.	Remarks.
1	8.0	14.2030	orange	strong	72.0°	semi-crystalline, soft
1A	8.0	14.3260	"	"	80.0°	" "
		Mean 14.2645				
2	16.0	13.7764	orange-brown	strong	100.0°	semi-crystalline, soft
2A	16.0	13.4370	deep orange	"	108.0°	" "
		Mean 13.6067				

No.	Weight H_2SO_4.	Weight of product.	Color.	Odor.	Melting-point.	Remarks.
3	24.0	15.0656	yellow	slight	129.5°	slightly crystal'e, hard
3A	24.0	15.7075	"	none	136.0°	" " "
		Mean 15.3866				
4	52.4	17.7699	light yellow	none	108.0°	no visible crystals, hard
4A	52.4	16.9200	"	"	110.0°	" " " "
		Mean 17.3449				

SET 3.—27.87 GRAMS OF NITRIC ACID USED CORRESPONDING TO FORTY GRAMS 34° B. ACID.

No.	Weight H_2SO_4.	Weight of product.	Color.	Odor.	Melting-point.	Remarks.
1	8.0	13.4895	orange	strong	84.0°	crystalline mass, soft
1A	8.0	14.2570	"	"	80.0°	" " "
		Mean 13.8733				
2	16.0	14.7964	deep orange	slight	97.0°	crystalline mass, soft
2A	16.0	15.0230	" "	"	94.0°	" " "
		Mean 14.9097				
3	24.0	16.2178	orange-yellow	none	133.0°	slight'y cryst'l, hard
4	52.4	16.3830	brown-yellow	none	126.0°	slight'y cryst'l, hard
4A	52.4	16.7150	light brown	"	126.0°	" " "
		Mean 16.5490				

SET 4.—20.90 GRAMS OF NITRIC ACID USED CORRESPONDING TO THIRTY GRAMS 34° B. ACID.

No.	Weight H_2SO_4.	Weight of product.	Color.	Odor.	Melting-point.	Remarks.
1	8.0	13.6220	orange	strong	99.0°	crystalline mass, soft
1A	8.0	13.6460	"	"	85.0°	" " "
		Mean 13.6340				
2	16.0	13.7861	yellow	none	122.0°	slightly crystalline, somewhat soft
2A	16.0	14.2410	"	"	....	slightly crystalline, hard.
		Mean 14.0136				
3	24.0	14.4400	choc'l-brown	none	106.0°	no visible crystals, hard
3A	24.0	14.9230	" "	"	108.0°	" " " "
		Mean 14.6815				
4	52.4	charred	....	....	....	tarry, semi-liquid
4A	52.5	charred	....	....	....	" "

The highest yield was therefore obtained in every set except No. 4, when an excess of sulphuric acid was used. In No. 4 so little nitric acid was present that the product was decomposed by the sulphuric acid. The degree of nitration, as characterized by

the melting-point, also increases with the amount of sulphuric acid present, but an excess has the opposite effect. The amount of nitric acid used in Set 1 has no advantage over the smaller amount used in Set 2, but it is not advisable to use still less acid, especially when higher nitration degrees are desired, since the product is apt to be attacked by the sulphuric acid.

To obtain nitro derivatives of naphthalene for commercial purposes, it is therefore best to nitrate the naphthalene with a mixture of nitric and sulphuric acids, using about three times as much 36° B. acid as naphthalene. The amount of sulphuric acid to be used will vary with the nitration degree desired and ranges from 4 : 1 (nitric : sulphuric) for low melting products, to 3 : 2 for the higher derivatives. Too large an excess must be avoided, as it chars the product, producing a tarry useless end-product.

WASHINGTON, D. C., MAY 13, 1897.

SPONTANEOUS COMBUSTION OF MOLASSES.

BY J. T. CRAWLEY.

Received April 5, 1897.

EARLY in September of last year a sample of charred molasses was forwarded to the laboratory of the Hawaiian Experiment Station from the Hamakua Mill, Hawaii, but owing to stress of work it was not examined until quite recently. The following extracts are taken from the letter from Mr. William McQuaid, chemist at the Hamakua Mill, which accompanied the sample. "The molasses in question was boiled to what is known as "string proof," at a temperature of 160°-165° F., and run into an underground cistern from time to time until the molasses was within six or eight inches of the top of the cistern, when the walls cracked, and the molasses began to leak out. The molasses continued to leak for about one and a half months, during which time five or six feet of the molasses was thus lost. That which remained seemed to be in a perfect condition. Five days later, however, it was found flowing over the sides of the cistern in somewhat of a burnt state. The temperature at the point where the molasses flowed over was 92° C., but in the cistern, and especially where the crack was located, this boiling seemed to be more violent.

"This flowing continued for about twelve hours, but the molasses continued boiling within the cistern until there was left

nothing but a few feet of charred mass. The fumes given off affected the eyes very much, and coming in contact with the metal roof formed a salt."

The sample of char formed under the above conditions was tested with a view of establishing the probable degree of heat at which the changes took place, as also to find the origin of the heat. Parts of the sample were quite black, having somewhat a ropy feel and consistency; other parts were dry, brittle, vesicular masses, brownish in color, resembling very much vesicular lava, while still other portions were of a much lighter color, the decomposition having gone so far as to drive off almost all volatile products, leaving a residue of carbon, ash, etc.

Several hundred grams of the material were repeatedly macerated and digested with cold and hot water. A large portion dissolved, giving a very dark colored solution, resembling the solution of caramels. This dark colored substance was still dissolved in notable quantities even after five days' digestion. The water solution was quite acid; therefore a weighed quantity was taken, digested with water, and the filtrate distilled with phosphoric acid. The acid of the distillate proved to be acetic acid almost entirely, with a small quantity of formic acid. The total acid amounted to three and eight-tenths per cent. calculated as acetic acid.

Sucrose.—500 grams were extracted with water, sufficient alcohol added to bring the strength of the alcoholic solution to sixty per cent., and precipitated with strontium oxide. The very copious precipitate was filtered, washed, suspended in water, and saturated with carbon dioxide. The filtrate from this precipitate was clarified with lead acetate, the lead thrown out with hydrogen sulphide, and the clear filtrate evaporated. Not a trace of sucrose could be detected either by crystallization or by reduction of copper solution after hydrolysis. This negative result was to be expected, since the large content of free acid taken in connection with the high heat during combustion in the tank, would have broken up the sucrose very quickly.

The distillate, obtained by distilling a portion of the original matter with phenyl hydrazine, gave the characteristic furfural hydrazone, thereby proving the presence of furfural in the original material, but in minute quantities.

On evaporating the water solution of the char, and adding alcohol, a very dense precipitate was obtained, which on purification and hydrolyzing with hydrochloric acid, reduced Fehling's solution, showing the presence of glucose-yielding bodies, or mucilages in comparatively small quantities.

The original sample, on being distilled with hydrochloric acid, gave with phenyl hydrazine the test for furfural-yielding bodies, the gums, in extremely small quantities, thus showing that these bodies, the mucilages and gums, have been almost totally destroyed. In the so-called gums found in the sugar-cane Dr. Maxwell found 64.6 per cent. to be glucose-yielding bodies, or hexosans, and 3.6 per cent. furfural-yielding bodies, or pentosans.

The water-soluble bodies present in the original char were separated by alcohol of different strength into bodies having melting-points varying from 130° C. to 275° C., while others decompose without melting.

The following bodies were detected, the per cent. being given where that was estimated :

Organic acid distilled	3.80 per cent. calculated as acetic acid.
Furfural	minute quantities
Furfural-yielding bodies	" "
Glucose-yielding bodies	small "
Caramels	large "

	Per cent.
Reducing sugars	11.20
Nitrogen	0.87
Phosphoric acid	0.30
Potash	2.27
Insoluble in water	38.20
Moisture	15.00

The moisture fumes given off from the burning mass came in contact with a metal roof and formed a salt, a sample of which also was forwarded to this office. The salt was almost pure zinc acetate with a little formate. The formic acid was separated from acetic by digesting their lead salts with alcohol, breaking up the insoluble lead formate with hydrogen sulphide and proving the presence of formic acid by its reducing action on silver and mercury salts.

Taking the original molasses from which this char resulted as having the probable composition,

	Per cent.
Water	20
Sucrose	45
Glucose	10

we see (1) that fully eighty per cent. of the sugars present have been destroyed, with a large part of the gums and mucilages; (2) that they have yielded, among other bodies, formic and acetic acid, the latter in large quantities, furfurol and caramels of varying degrees of solubility and melting-points; and (3) that a residue of insoluble caramels and unburnt carbon largely, to the amount of fully one-third the weight of the char is left behind.

As to the degree of heat at which these changes took place, we must conclude that at least a temperature of 200° C. was maintained for some time during which the caramel was formed, while a very much higher degree was reached toward the end of the action.

The phenomenon can have been nothing else than spontaneous combustion, the acid products being oxidation products, and therefore having lower thermal values than the original sugars. The successive stages of oxidation and decomposition furnished the heat necessary to carry the whole mass to the next stage.

As to the initial cause of the rise in temperature, little can be said; the high water content and known fluidity of molasses would tend to retard decomposition by oxidation. It is a fact well known among practical sugar-house men, that if a molasses of low grade be boiled at a high temperature and run into coolers it is very apt to froth and foam, and run over the sides of the containers. It is also known that running successive charges of hot molasses into the same container will often result in a burning of the product and foaming over the sides of the container.

The cause of this foaming and frothing is not positively known. Fermentation often proceeds in a very thick molasses, in fact at a much higher density than is generally known, and the escaping carbon dioxide would tend to cause the mass to rise up. I am inclined to believe, however, that in the majority of

cases this frothing is due to decomposition of the non-sugars. This is a subject that will be looked into.

Whatever may have been the initial cause of heat, whether fermentation or decomposition due to the treatment, there can be no doubt that there was a violent manifestation of heat most destructive in its effects.

THE FERROCYANIDES OF ZINC AND MANGANESE.[1]

By G. C. Stone and D. A. Van Ingen.

Received May 15, 1897.

OUR work on ferrocyanides was undertaken more to try to reconcile the very discordant statements that have been made about its value as a means for the volumetric determination of zinc than to determine the exact composition of the salts. We therefore have merely tried to determine the influence of temperature and acidity on the composition of the precipitates formed when potassium ferrocyanide is added to the solution of a salt of zinc or manganese. The simplest method for this is to add to a known amount of a zinc solution an excess of a ferrocyanide solution, the strength of which has been accurately determined by titration with permanganate and to determine the excess of ferrocyanide not precipitated by the zinc by titration with permanganate. We found that it was practically impossible to filter the ferrocyanides of either zinc or manganese, but by diluting to a known volume, allowing the precipitate to settle and titrating an aliquot portion, we obtained results that agreed with each other, provided the excess of ferrocyanide remained the same; but with varying excesses the ratio of zinc to ferrocyanogen in the precipitate fell irregularly as the excess of ferrocyanide increased. With manganese this method also failed, as we found that the ferrocyanides of manganese were somewhat soluble in water, rather more so in potassium ferrocyanide and entirely soluble in strongly acid solutions.

We next tried precipitating zinc and manganese in neutral, strongly acid solutions, both hot and cold, and in cold slightly acid ones. The precipitates were washed by decantation. Most of them settled very slowly, especially when nearly washed. We found that they settled much more rapidly if some other salt

[1] Read at the meeting of the New York Section, May 7, 1897.

was present, and in most cases added barium chloride, as it caused the precipitate to settle comparatively rapidly and did not react with it. Even then the washing was very tedious, requiring several days. The zinc salts were much easier to wash than the manganese, and it was possible to test the completeness of the washing, as they are not appreciably soluble in water; but with manganese it was impossible to tell when the washing was complete, owing to the solubility of the manganese ferrocyanides. We therefore washed all the manganese precipitates several times more than we found necessary for the zinc, but even then felt somewhat doubtful of the result in some cases.

We found the best test for soluble ferrocyanides was a very dilute solution of cobalt nitrate, so dilute that two or three drops of it on a white porcelain plate showed no color. In applying the test the best way is to put a drop of a dilute solution of cobalt on a watch-glass and shake it off so that only a very minute drop, or no visible *drop* remains, then add two or three drops of water and a few drops of the solution to be tested. Hold the watch-glass at about the level of the eye and look across the surface towards a window; a faint green can be seen if even a trace of ferrocyanide is present. If the cobalt solution is not very dilute, its color, red, neutralizes the green, and it does not show. Testing the delicacy of this reaction with known amounts of ferrocyanide, we found that one cc. of a solution containing 0.000009 gram of potassium ferrocyanide showed a color, when compared with distilled water; but with one containing 0.000007 gram no color could be seen. Ferric chloride is nearly, but not quite, as delicate as cobalt; uranium is much less delicate.

Having washed our precipitates, we dried them and heated a weighed portion in a porcelain crucible, at first gently, then very strongly, to decompose the organic matter; dissolved in hydrochloric acid and boiled with potassium chlorate to oxidize the iron; precipitated the iron by barium carbonate; dissolved the precipitate; reduced the iron by hydrogen and determined it by titration with potassium permanganate. In the filtrate from the iron we determined the manganese by titration with permanganate. The zinc we separated from the excess of barium by pre-

cipitation as sulphide, converted to phosphate and weighed as pyrophosphate; or, we removed the barium as sulphate and determined the zinc as pyrophosphate in the filtrate. The atomic weights used were those given in this Journal, **18**, 213 (March, 1896), where oxygen equals 16. They are: Carbon, 12.01; hydrogen, 1.008; iron, 56.02; manganese, 54.99; nitrogen, 14.04; phosphorus, 31.02; potassium, 39.11; and zinc, 65.41. We did not attempt to determine more than the ratio of zinc or manganese to iron, which, of course, is the same as the ratio of ferrocyanide.

A zinc salt precipitated from a neutral solution in the cold, the amount of ferrocyanide used being slightly in excess of what was required to form zinc ferrocyanide with the zinc present, gave a ratio of 287 atoms of zinc to 285 atoms of iron. A second similar precipitate gave a ratio of 702 : 692. In both cases the ratio is practically 1 : 1, giving the empirical formula $ZnK_2Fe(CN)_6$.

Two lots precipitated from cold neutral solutions, in which the zinc was in excess, gave ratios of 501 : 511, and 700 : 684, which also gives the formula $ZnK_2Fe(CN)_6$.

The next precipitate was formed in a cold solution containing five cc. per hundred of hydrochloric acid. Two portions of this were analyzed giving ratios of 160 : 113 and 318 : 227, or in both cases 100 : 71, this would make the formula $Zn_{10}K_8(Fe(CN)_6)_7$, about an average of two of the other salts found.

The next two were precipitated from hot solutions, *A* was neutral and *B* contained five cc. of hydrochloric acid per hundred. *A* gave a ratio of 189 : 136, and *B* of 176 : 135; in both cases nearly 4 : 3, making the formula $Zn_4K_4(Fe(CN)_6)_3$.

We precipitated the next lot in a dilute solution containing one cc. of dilute (1 : 6) hydrochloric acid in each hundred, these being the conditions under which we precipitate zinc and manganese in the volumetric method we use. This gave us ratios of 175 : 131 and 174 : 130, giving the formula $Zn_4K_4(Fe(CN)_6)_3$.

The last zinc salt which we analyzed was bought from a dealer in chemicals as $Zn_2Fe(CN)_6$. It gave us ratios of 169 : 115 and 170 : 116, giving the formula $Zn_3K_2(Fe(CN)_6)_2$.

With manganese the results were not quite as satisfactory, owing to the impossibility of being sure that the precipitates

were completely washed. In the precipitates that received the most washing we found the simplest ratios of manganese to iron.

Two lots precipitated from cold neutral solutions, *A* containing more and *B* less ferrocyanide than would form $Mn_2Fe(CN)_6$, gave ratios of, *A* 555 : 594, and *B* 941 : 991, slightly more than 1 : 1, making the formula $Mn_{20}K_{44}(Fe(CN)_6)_{21}$, or more probably $MnK_2Fe(CN)_6$.

The next were precipitated from cold solutions containing five cc. of hydrochloric acid per hundred; they gave ratios of 155 : 116 and 309 : 233, or 4 : 3, making the formula $Mn_4K_4(Fe(CN)_6)_3$.

The next solutions were hot, *A* containing five cc. hydrochloric acid per hundred and *B* being neutral. The ratios were: *A* 148 : 161, and *B* 144 : 135, giving the formula $Mn_{10}K_{24}(Fe(CN)_6)_{11}$, and $Mn_{20}K_{36}(Fe(CN)_6)_{19}$; in both cases it should probably be $MnK_2Fe(CN)_6$.

The last of the manganese salts were prepared under the conditions we have in our volumetric method, a cold solution containing one cc. of dilute (1 : 6) hydrochloric acid in one hundred cc. They gave ratios of 141 : 140 and 142 : 140—$MnK_2Fe(CN)_6$.

It being evident from the preceding that both zinc and manganese form different salts under varying conditions, we next tried whether the different indicators which have been proposed for volumetric analysis showed the same salt, and whether any one indicator showed different salts under different conditions. The indicators which we have seen proposed are ferric salts, uranium, cobalt, copper, and platinum. In testing we used zinc and manganese solutions, in which the metals had been very carefully determined gravimetrically, and a solution of potassium ferrocyanide which had been titrated with permanganate, and the ferrocyanide value calculated from the iron value. The variables were the proportions of acid, the temperature, the dilution of the indicator, and the way the solution and indicator were brought together.

In a cold solution containing one-seventh cc. of hydrochloric acid in one hundred, uranium, when a drop of it was mixed with a drop of the solution on a porcelain plate, showed the reaction when the quantities of zinc and ferrocyanide were sufficient to form $Zn_2Fe(CN)_6$.

In a hot solution containing ten cc. of hydrochloric acid,

uranium, used as in the last case, gave the reaction with $Zn_3K_2(Fe(CN)_6)_2$.

In a cold solution containing one-seventh cc. of acid, uranium gave a reaction for $Zn_4K_4(Fe(CN)_6)_3$, when drops of it and the solution were placed side by side on filter paper so that the uranium did not touch the precipitate, but only the clear solution that filtered from it. Under the same conditions copper and ferric chloride gave the reaction at the same point.

Cobalt was tried, using a strong solution, placing a drop on porcelain and a drop of the solution by it, so that the two touch, but do not mix. The reaction was for $Zn_4K_4(Fe(CN)_6)_3$. When the solution was *mixed* with *very* dilute cobalt, the reaction was for $Zn_3K_2(Fe(CN)_6)_2$. Both of the solutions tested with cobalt were cold and contained one-seventh cc. hydrochloric acid per hundred.

Platinum was not tried. Dr. Miller[1] states that when used with a hot acid solution it gives the reaction with $Zn_3K_2(Fe(CN)_6)_2$. He says it does not work with a cold solution.

With manganese we tried only three indicators. In all cases the solutions were cold and contained one-seventh cc. of hydrochloric acid per hundred. Strong cobalt and uranium on paper gave the reaction for $MnK_2Fe(CN)_6$; very dilute cobalt gave it for $Mn_3K_2(Fe(CN)_6)_2$.

Of the different indicators tried we found cobalt the most satisfactory, as it shows the reaction as soon as the drops touch, while all the others require an appreciable time for it to develop.

It will be seen that all the salts shown by the indicators, all but the third of the zinc series, and, we may add, twenty-three out of twenty-eight, in which we tried to determine the ratios by adding an excess of ferrocyanide and titrating it, are salts having nearly the general formula $K_4Fe(CN)_6, nR''_2Fe(CN)_6$, which is possibly the formula of these salts. Nearly all of those which contain more than one atom of the heavy metal agree fairly with the formula $R_n K_{2n-4} (Fe(CN)_6)_{n-1}$, the salt with one atom being the common difference of the series $R''K_2Fe(CN)_6$. It would, of course, require much more work than the limited time at our disposal has permitted to establish the correctness of either.

[1] This Journal, 18, 1100.

In using ferrocyanide as a reagent for volumetric analysis, it is of the utmost importance to keep all of the conditions absolutely uniform. Provided this is done the results are good, but if there is any variation they are liable to be entirely incorrect.

The following table gives the analytical results in detail:

TABLE.

Excess.	Hydrochloric acid. cc.	Temperature.	Zinc. Grams.	Iron. Grams.	Zinc. Atoms.	Iron. Atoms.	Zn : Fe : : 100 :
$Fe(CN)_6$	0	Cold	0.01875	0.01596	287	285	99
$Fe)CN)_6$	0	"	0.04598	0.03878	702	692	98
Zn	0	"	0.03280	0.02866	501	511	102
Zn	0	"	0.04579	0.03831	700	684	98
$Fe(CN)_6$	5	"	0.10500	0.06368	160	113	70
$Fe(CN)_6$	5	" (*a*)	0.42268	0.05098	318	227	71
$Fe(CN)_6$	0	Hot	0.12392	0.07616	189	136	72
$Fe(CN)_6$	5	"	0.11500	0.07575	176	135	76
$Fe(CN)_6$	$\frac{1}{7}$	Cold	0.11469	0.07367	175	131	75
$Fe(CN)_6$	$\frac{1}{7}$	"	0.11414	0.07287	174	130	75
Bought as $Zn_2Fe(CN)_6$			0.11053	0.06497	169	115	78
Bought as $Zn_2Fe(CN)_6$			0.11157	0.06508	170	116	67
			Manganese. Grams.		Manganese. Atoms.		Mn : Fe : : 100 :
$Fe(CN)_6$	0	Cold	0.03050	0.03330	556	594	107
Mn	0	"	0.51763	0.55500	941	991	105
$Fe(CN)_6$	5	"	0.08522	0.06540	155	116	75
$Fe(CN)_6$	5	" (*b*)	0.03408	0.05252	309	233	75
$Fe(CN)_6$	5	Hot	0.08139	0.09010	148	161	109
$Fe(CN)_6$	0	"	0.07938	0.07547	144	135	94
$Fe(CN)_6$	$\frac{1}{7}$	Cold	0.07757	0.07844	141	140	99
$Fe(CN)_6$	$\frac{1}{7}$	"	0.07788	0.07862	142	140	99

(*a*) Zinc and iron determined in different portions.

(*b*) Manganese and iron determined in different portions.

[CONTRIBUTION FROM THE ANALYTICAL LABORATORIES OF COLUMBIA UNIVERSITY.]

ON THE FERROCYANIDES OF ZINC AND MANGANESE.[1]

BY EDMUND H. MILLER AND J. A. MATHEWS.

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INTRODUCTION.

THE work to be described was undertaken to determine whether the precipitates formed by adding potassium ferrocyanide to solutions of zinc or manganese are normal ferrocyanides, as given by many authorities, or double potassium ferro-

[1] Read at the meeting of the New York Section, May 7, 1897.

cyanides, as suggested in a preliminary article which appeared in this Journal last December, and also whether the composition of the precipitate is the same if an excess of precipitant be added. The delays encountered in the course of the work made it necessary to confine ourselves to the precipitates formed in the cold, in solutions slightly acidified with hydrochloric acid, as these seemed the most important conditions on account of the solubility of the manganese ferrocyanide in hot solutions, and also on account of the zinc; for if we can establish the composition of the precipitate when formed in the cold to be $K_2Zn_3(Fe(CN)_6)_2$ we have the results of the standardizing of thousands of ferrocyanide solutions to prove it the same when hot.

Preparation of the Ferrocyanides. — A strong solution of zinc chloride was prepared by dissolving pure granulated zinc in hydrochloric acid, so that but a slight excess of acid remained; this was diluted and placed in two large bottles. To one portion potassium ferrocyanide was added so as to leave the zinc in excess. This was thoroughly mixed, and the presence of an excess of zinc chloride confirmed by testing with ferric chloride. The precipitate was white, flocculent, and showed at first a tendency to settle. It was washed by decantation with water seven times, the clear supernatant liquid being removed by a siphon and the precipitate thoroughly agitated with the water added. After the seventh washing no chlorides were present. The precipitate was then transferred to a filter, washed again, and then dried at 95° C. (Sample *A*.)

To the second portion an excess of potassium ferrocyanide was added and the solutions thoroughly mixed. An excess of ferrocyanide was found to be present by testing with ferric chloride. The precipitate was white, flocculent, and settled well at first, but after washing settled more slowly. It was washed six times, as already described, except that after several washings alcohol was added with the water to hasten the settling of the precipitate. This aided somewhat, but the process is not rapid, as the washing of this precipitate required eight weeks. After the sixth washing the liquid gave no test for ferrocyanide. It was not found possible to filter this zinc ferrocyanide, so it was left in the bottle and samples taken direct for the determination of the ratio of zinc to iron. (Sample *B*.)

Manganese ferrocyanides were prepared as follows: To a concentrated aqueous solution of manganous chloride, acidified with hydrochloric acid, potassium ferrocyanide was added so as to leave the manganese in excess. The precipitate was greenish white and flocculent, but settled slowly. It was washed with water several times, as already described. At first the precipitate ran through the filter paper, but on standing for several weeks it became more flocculent and filtered well. After filtering it was dried in an air-bath below 100° C. This ferrocyanide, when dried, has a slate color. (Sample *C*.)

Another portion of manganous chloride was mixed with an excess of ferrocyanide solution and allowed to stand. The precipitate scarcely settled at all, so after waiting several weeks and making several incomplete decantations, alcohol was added with the water which effected a more rapid separation. It was washed seven times; the last wash water was free from ferrocyanide, but contained a trace of chloride. The washing of this precipitate required many weeks. (Sample *D*.) This sample was not dried but kept for the determination of ratios only. On boiling a portion of this ferrocyanide it became dark blue and more flocculent, evidently undergoing decomposition. The hydrochloric acid present in each case was about one cc. of 1.20 sp. gr. The temperature was 23° C.

These ferrocyanides have a most remarkable affinity for water. Attempts were made to determine the water present in Sample *C* by drying it in an air-bath. Eleven weighings were made at intervals of from one to two hours, at increasing temperatures from 102° C. to 150° C., but no constant weight was reached. On cooling, water was again absorbed. The avidity for moisture is so great that the tube containing the precipitate, though tightly corked, was found to steadily increase in weight. When water is added to these ferrocyanides, dried at 100° C., it is taken up with a crackling sound and a marked evolution of heat.

To avoid error from the absorption of moisture the following method was adopted: The tube containing the sample dried at 100° C. was weighed, then a portion shaken out into a platinum boat and the tube recorked, allowed to assume a constant weight, and reweighed. The boat containing the sample was imme-

diately placed in a glass tube in a combustion furnace, heated in a current of dry air till the sample began to char; and the water absorbed by calcium chloride. While this determination was in progress five or six portions for analysis were weighed out into small beakers by difference, then another portion was weighed into a boat as before and the moisture again determined. The average of the two percentages of moisture was used in calculating the intermediate portions to the dry basis. The percentages so obtained never varied more than one-quarter of a per cent.

Sample *A*.—Zinc chloride in excess contained: water 9.41 and 9.33 per cent., average used 9.37 per cent.

Sample *C*.—Manganous chloride in excess contained: water 3.35 and 3.11 per cent, average 3.23 per cent. Other determinations made after redrying at 100° C., after an interval of about one month, gave water 3.50 and 3.32 per cent., average 3.41 per cent., showing that the sample when dried at 100° C. has a nearly constant amount of water.

Wyrouboff[1] assigns to the manganese ferrocyanide four molecules of water, corresponding to 2.28 per cent. We have found that, when dried from 145° to 148° C., from 2.26 to 2.36 per cent. loss in weight results, but do not believe the compound contained any definite water of crystallization. He gives to the zinc ferrocyanide twelve molecules of water, or 13.40 per cent. This result we have not confirmed.

We do not believe any further evidence is necessary to prove that these ferrocyanides are without water of crystallization.

Methods of Decomposition.—The ignition method given by Wyrouboff was tried in connection with the determination of potash, but the results were found to be low and irregular as the resulting oxides adhered to the platinum and the potash could not be leached out completely.

Rose's method for the determination of cyanogen, as given by Fresenius, was tried on the zinc ferrocyanide but without satisfactory results. Three portions were digested with silver nitrate, adding a few drops of nitric acid from time to time, and the resulting silver cyanide weighed on balanced filters. The percentages of cyanogen were: 44.63, 44.83, and 44.12, which

[1] Ann. phys. Chem. (5), **8**, 474, 485.

agreed well with the calculated percentages of $Zn_3K_2(Fe(CN)_6)_2$, which is 44.70, but it was found that the iron in the filtrate was invariably low and that when the precipitate of silver cyanide was scorified with test lead and cupelled, the silver resulting corresponded to only about 35 per cent. of cyanogen, showing an incomplete decomposition of the ferrocyanide.

Decomposition by means of concentrated sulphuric acid was tried with satisfactory results, except for the separation of small quantities of carbon, which had a tendency to climb up the sides of the casserole.

The method finally adopted, and which we consider entirely satisfactory, is as follows: Add to the casserole containing about one gram of the ferrocyanide, ten to fifteen cc. of concentrated nitric acid, and heat till the action is over and no more nitrous fumes are seen; cool, rinse down the sides of the casserole with water, add about twenty cc. of concentrated sulphuric acid, and boil, holding the casserole over the flame and, keeping the contents constantly in motion, until copious fumes of sulphuric acid are evolved, cool, and again rinse down the sides. At this point a decided blue color usually appears as some of the ferrocyanide which adheres to the sides of the vessel escapes decomposition; add more sulphuric acid and repeat the operation till nearly all of the sulphuric acid has been driven off; cool, dilute again, and, if no blue color appears, add a few drops of hydrochloric acid to dissolve the ferric sulphate and the solution is ready for analysis. The addition of nitric acid prevents any separation of carbon. In spite of these precautions, however, we have sometimes found traces of iron in the ferrous condition which required subsequent oxidation.

ANALYSIS OF THE ZINC FERROCYANIDES.

Sample A.—Zinc chloride in excess. Determination of zinc and iron. 0.9322 gram of the precipitate dried at 100° C. was decomposed, as already described; the iron was precipitated as basic acetate, washed, then the precipitate dissolved in hydrochloric acid and twice precipitated by ammonia. The precipitate of ferric hydroxide was dissolved in hydrochloric acid, reduced by stannous chloride, and titrated by potassium permanganate according to the Zimmerman-Reinhart method. The filtrates containing zinc were combined, acidified with acetic acid, and

the zinc precipitated as sulphide in a hot solution. The zinc sulphide, after washing, was dissolved in nitric acid, a decided excess of a saturated solution of microcosmic salt added, the solution boiled and then neutralized with ammonia, and allowed to stand on a water-bath till only a trace of ammonia remained; when cold the zinc ammonium phosphate was filtered and weighed on balanced papers after drying at 100° C. The results were: iron 16.11 per cent., zinc 27.93 per cent. A duplicate determination of iron gave 16.07 per cent.

The zinc was also determined by decomposing the ferrocyanide by potassium hydroxide, then precipitating by hydrogen sulphide, and finally, as zinc ammonium sulphate. The method gave 27.60 per cent. of zinc.

For the determination of potassium 0.5360 gram was decomposed as usual, the iron precipitated by ammonia, then the zinc by hydrogen sulphide, the filtrate acidified with sulphuric acid, and evaporated to dryness and ignited in a platinum dish. The potassium sulphate weighed 0.1208 gram, corresponding to 11.14 per cent. of potash when calculated to the dry basis.

Sample B.—Ferrocyanide in excess. On account of the difficulty of filtering and because the presence of potassium is already proved, only the ratio of iron to zinc was determined in this case. Portions, judged to contain about one gram of the dry compound, were transferred to casseroles as before and the alcohol driven off on the water-bath. The sample was then decomposed as usual and the zinc determined as already described. The iron was weighed as Fe_2O_3. The results were as follows:

Iron to zinc	1 : 1.4000
" " "	1 : 1.4088
" " "	1 : 1.3903
Average	1 : 1.3997

The following table shows a comparison of our results with the theory calculated for $Zn_3K_2(Fe(CN)_6)_2$ and with the analytical results of Wyrouboff. The percentages of cyanogen are calculated from the iron:

	Miller and Mathews. Per cent.	Mathews. Per cent.	Wyrouboff. Per cent.	Theory. Per cent.
Cyanogen.....	44.87	44.75	46.97	44.70
Iron	16.11	16.07	16.86	16.02
Zinc	27.93	27.60	27.48	28.07
Potassium	11.14	....	10.51	11.20
	100.05		101.82	99.99

Our results agree very closely with the theory and agree perfectly with the results obtained by titration when uranium acetate is used as an indicator. The ratio of iron to zinc is 1 : 1.49, compared to the theory 1 : 1.500, while Wyrouboff's is 1 : 1.395. This ratio coincides almost exactly with the proportions we found when the ferrocyanide was in excess (Sample *B*), and shows that Wyrouboff came to the conclusion that the precipitate was the same whichever was in excess on account of the inaccuracy of his analytical results.

The ratios obtained from Sample *B*, ferrocyanide in excess, correspond to a formula containing 5 iron and 7 zinc, which would be $Zn_7K_6(Fe(CN)_6)_5$.

COMPARISON OF RESULTS.

Theory, iron to zinc	1 : 1.4000
Miller and Mathews, iron to zinc	1 : 1.3997
Wyrouboff, iron to zinc.....	1 : 1.3955

ANALYSIS OF THE MANGANESE FERROCYANIDE.

Sample C.—Manganous chloride in excess. Portions of about one gram each were decomposed by nitric and sulphuric acids, in the same way as the zinc ferrocyanide, then dissolved in hydrochloric acid and water, as before. The manganese and iron were determined in the same portion as follows: The iron was precipitated twice as basic acetate, then by ammonia, and weighed as Fe_2O_3. The filtrates and washings from the two basic acetate precipitations were combined, concentrated, and the manganese precipitated by bromine after adding sodium acetate, etc.; the oxide of manganese, MnO_2, was dissolved in hydrochloric and sulphurous acids, and precipitated as manganese ammonium phosphate in the ordinary manner. The manganese was ignited and weighed as pyrophosphate.

The method used for the determination of potassium was the

same as described under zinc except that the manganese was precipitated in an ammoniacal, not an acetic acid solution.

The results calculated to the dry basis are as follows: Iron 16.36 and 16.40 per cent., manganese 17.67 and 17.67 per cent., potassium 20.33 and 19.64 per cent.

Other determinations of manganese and iron in the same portion gave the following ratios:

Fe : Mn : : 1 : 1.1039, and as 1 : 1.1080.

Sample D.—Ferrocyanide in excess. On account of the perverse character of this precipitate only the ratio of iron to manganese was determined. The method of decomposition and analysis has already been described. The results are as follows:

Fe : Mn : : 1 : 1.0502
Fe : Mn : : 1 : 1.0623
Fe : Mn : : 1 : 1.0758

The following table gives a comparison of our results with the theory calculated from Wyrouboff's formula without the water of crystallization, $5Mn_2Fe(CN)_6$, $4K_4Fe(CN)_6$ and with his own results. The cyanogen is calculated from the iron:

	Miller and Mathews. Per cent.	Per cent.	Wyrouboff. Per cent.	Theory. Per cent.
Cyanogen	45.57	45.68	45.44	45.52
Iron	16.36	16.40	16.31	16.34
Manganese.....	17.67	17.67	18.19	17.89
Potassium.....	20.33	....	19.35	20.23
	99.93		99.29	99.98

These results agree very fairly with the theory for Wyrouboff's formula, but still better with a ratio of 10 iron to 11 manganese, as will be seen from the following ratios:

Fe : Mn : : 1 : 1.099
Fe : Mn : : 1 : 1.097
Fe : Mn : : 1 : 1.104
Fe : Mn : : 1 : 1.108

Average 1 : 1.102
Theory for 10 Fe : 11 Mn, 1 : 1.100

While these results agree most perfectly with a ratio of 10 to

11, we do not wish to advance a corresponding formula, as the difference between this ratio and the 9 to 10 of Wyrouboff is very slight and the composition of the precipitate very readily affected by slight changes in the conditions of precipitation. The average of three ratios of iron to manganese determined on Sample *D*, ferrocyanide in excess, is 1 : 1.0628, corresponding to a formula containing 16 iron to 17 manganese. We do not give to this ratio its appropriate formula, as the precipitate may be a mixture of two simple ferrocyanides, but we believe that a comparison of these ratios shows that the manganese precipitate does not have the same composition whether manganese or ferrocyanide is in excess, as stated by Wyrouboff.

The physical properties of this precipitate confirm the fact that it readily undergoes a change in composition, for if a solution of potassium ferrocyanide is poured into one of manganous chloride it first is pinkish white, on adding more ferrocyanide it becomes greenish, and when the ferrocyanide is in excess a light slate color.

The conclusions arrived at by us are :

First.—The precipitates formed by potassium ferrocyanide and chloride of zinc or manganese are double ferrocyanides and not normal ferrocyanides, as given by Prescott and Johnson[1] and by Stone.[2]

Second.—The ferrocyanides formed when the metal is in excess does not contain water of crystallization, as given by Wyrouboff.[3]

Third.—The precipitate formed in a dilute hydrochloric acid solution of zinc chloride by potassium ferrocyanide when the zinc chloride is in excess, is $Zn_3K_2(Fe(CN)_6)_2$ as given by Wyrouboff.[3]

The precipitate is not the same whichever is in excess. When ferrocyanide is in excess the ratio of iron to zinc is as 1 to 1.40, which corresponds to $Zn_7K_6(Fe(CN)_6)_5$.

Fourth.—The manganese precipitate formed when manganese chloride is in excess agrees well with the formula $5Mn_2Fe(CN)_6$, $4K_4Fe(CN)_6$, as given by Wyrouboff, but better with a ratio of 10 iron to 11 manganese. When the ferrocyanide is in excess the

[1] Qual. Anal., pp. 57 and 67.
[2] This Journal, 17, 473.
[3] Am. Chim. Phys. (5), 8, 474, 485.

composition is different, corresponding to a ratio of 16 iron to 17 manganese. The manganese precipitate is very readily affected by changes in the conditions of precipitation.

In regard to the bearing of these results on the methods in use for the titration of zinc and manganese by potassium ferrocyanide, we believe the accuracy of the ordinary method of titrating zinc in a dilute hydrochloric acid to be confirmed and that the following reaction takes place:

$$2K_4Fe(CN)_6 + 3ZnCl_2 = Zn_3K_2(Fe(CN)_6)_2 + 6KCl.$$

The difference in the composition of the precipitate when ferrocyanide is in excess explains why all attempts to add an excess of ferrocyanide and titrate back by permanganate have failed.

The complicated and variable character of the manganese precipitate constitutes a serious objection to the method of determining manganese by potassium ferrocyanide, for aside from the difficulties arising from the solubility of the manganous ferrocyanide and its consequent action on indicators, the titration must be conducted under very carefully regulated conditions to give satisfactory results.

DISCUSSION ON THIS AND THE PRECEDING PAPER.[1]

Mr. Miller: All of these ferrocyanides can be resolved into two ferrocyanides having simple ratios, as follows:

Zinc in excess:

$$Zn_3K_2(Fe(CN)_6)_2 = ZnK_2Fe(CN)_6 + Zn_2Fe(CN)_6.$$

$K_4Fe(CN)_6$ in excess:

$$Zn_7K_6(Fe(CN)_6)_5 = 3ZnK_2Fe(CN)_6 + 2Zn_2Fe(CN)_6.$$

Manganese in excess:

Ratio of 11Mn to 10 Fe $= 9MnK_2Fe(CN)_6 + Mn_2Fe(CN)_6.$

$K_4Fe(CN)_6$ in excess:

Ratio of 17Mn to 16Fe $= 15MnK_2Fe(CN)_6 + Mn_2Fe(CN)_6.$

The explanation may be as follows: The acid in solution (HCl) reacting on the potassium ferrocyanide gives free hydro-

[1] NOTE BY THE EDITOR.—The Publication Committee have decided to publish the discussion on this and the preceding paper inasmuch as it seems to throw some additional light upon the subject. Hereafter such discussions, if published, will appear in the Proceedings.

ferrocyanic acid, which precipitates the normal ferrocyanide,[1] liberating in turn free acid, which continues the reaction. In this way a little acid can effect a great change in the composition of the precipitate.

If this theory is correct in a neutral solution, $ZnK_2Fe(CN)_6$ and $MnK_2Fe(CN)_6$ should be formed, while the proportions of zinc or manganese to potassium ferrocyanide remaining the same the greater the quantity of acid the more of the normal ferrocyanide $R_2Fe(CN)_6$ should be formed. This may be complicated, however, by the solubility of the manganese compound.

Expressed briefly, as the acid increases, the manganese or zinc in the ratio increases, and as the ferrocyanide increases, the zinc or manganese in the ratio diminishes.

This view of the composition and conditions for formation of these precipitates has received most important confirmation from the work of Stone and Van Ingen, for as I had expected they have found the two salts, $K_2MnFe(CN)_6$ and $K_2ZnFe(CN)_6$, to be formed in a cold neutral solution. The compound $K_4Mn_4(Fe(CN)_6)_3$ and $K_4Zn_4(Fe(CN)_6)_3$ also agree with this theory, for they may be resolved into $R_2Fe(CN)_6.2K_2RFe(CN)_6$ and are formed in an exceedingly dilute acid solution and occupy a position intermediate between the $K_2ZnFe(CN)_6$ of the neutral solution, and the $Zn_3Fe(CN)_6.K_2ZnFe(CN)_6$ obtained when more hydrochloric acid is present.

It must be admitted that these precipitates are extremely sensitive to changes of condition, but we have in uranium acetate an indicator which in an acid solution shows with certainty $Zn_3K_2Fe(CN)_6$, and according to Stone and Van Ingen we have in dilute cobalt nitrate an indicator which turns at $K_4R_4(Fe(CN)_6)_3$.

Mr. Van Ingen: I know that in carrying out the work of Mr. Stone, in obtaining a precipitate for analysis, there were two or three cases in which decomposition took place, and we had a ferrocyanide of iron formed, not shown by the strong blue color in the precipitate.

Another matter: a very curious changing in color took place during the washing of the manganese precipitate where we had manganese in excess and not where we had ferrocyanide in excess. It would start out sometimes with dark purple, from dark purple

[1] Wyrouboff: Ann. phys. Chem. (5), 8, 474.

to a dark pink, and gradually washing out until we ended with a pale slate color, and the solubility made it very hard to know just when we got through, because the cobalt tests would show ferrocyanide to the very end. All the precipitates were washed in bulk of 6,700 cc., allowed to settle in bottles, then siphoned off as far as possible, and water added. Most of them had from twenty to thirty washings, and by adding barium chloride we were enabled to get four or five washings a day. Before doing that, we were well satisfied with one washing in two days. As you continue, the washing and settlings get slower and slower, but there seems to be some very curious change in the manganese salts during this washing. The precipitate changed color in parts entirely during the washing.

Mr. Miller: There is a difference in color where the manganese or ferrocyanide is in excess and you get changes in color going from one washing to another.

Mr. Van Ingen: I was referring to washing the precipitate where manganese was in excess. We started with pinkish purple and ended up with a slate color.

Mr. Miller: I don't remember seeing a purple color, but I noticed a change from pinkish to sort of slate color.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

HALIDES AND PERHALIDES OF PYRIDINE.[1]

BY P. F. TROWBRIDGE AND O. C. DIEHL.

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ACTION OF BROMINE UPON IODIDES OF PYRIDINE.

Pyridine Hydriodide Dibromide, $C_5H_5N.HI.Br_2$, or $C_5H_5N.HBr.IBr$.—Reddish-brown, thin laminae or large, prismatic plates. Melting-point 172°–175° C. Very soluble in alcohol, with difficulty in chloroform, and scarcely at all in water. The samples for analysis were crystallized from alcohol.

Pure pyridine hydriodide was dissolved in water and brominated by passing carbon dioxide through bromine and then through the solution. At first a very dark red precipitate formed which appeared to be nearly pure iodine. Upon continued bromination the precipitate became brownish yellow,

[1] Continuation of previous paper. This Journal, 19, 322.

flocculent, and readily floated in the liquid. Gradually the precipitate became heavier and finally settled as a dark brown, viscous mass. A small amount of heat was generated during the bromination. Upon standing the precipitate became crystalline and the solution showed the presence of some iodine. The pure product was obtained by several crystallizations from alcohol.

	Calculated for $C_5H_5N.HI.Br_2$.	Found. I.	Found. II.
Titrated halogen	43.59	43.47 43.41	43.03
Total halogen	78.01	77.82 78.12	....

Pyridine Methyl Iodide Dibromide, $C_5H_5N.CH_3I.Br_2$, or $C_5H_5N.CH_3Br.IBr$.—Bright orange-yellow crystals, soluble in alcohol and acetone, does not crystallize well from the latter, insoluble in water and ether. From an absolute alcohol solution orange-yellow, short, prismatic, needle-like crystals were obtained. Melting-point 61°–62° C.

A water solution of pure pyridine methyl iodide was brominated in the same manner as the pyridine hydriodide. A heavy reddish brown oil formed, having a strong bromine-like odor. Potassium hydroxide decomposes the oil. When the oil is heated on the water-bath for several hours the bromine odor disappears and the oil becomes lighter in color. On cooling it forms a bright-orange crystalline mass. This was purified from alcohol.

	Calculated for $C_5H_5N.CH_3I.Br_2$.	Found.
Titrated halogen	41.96	41.53
Total "	75.26	75.04

Pyridine Ethyl Iodide Dibromide, $C_5H_5N.C_2H_5I.Br_2$, or $C_5H_5N.C_2H_5Br.IBr$.—Orange-yellow crystals, soluble in alcohol. Melting-point 25°–26° C.

This preparation was made by aspirating air through bromine and into a water solution of pure pyridine ethyl iodide. A dark red oil formed, which was separated from the liquor (no iodine found in liquor), and heated for a time on the water-bath. The oil was then purified by dissolving in alcohol.

	Calculated for $C_5H_5N.C_2H_5I.Br_2$.	Found. I.	II.
Titrated halogen	40.49	{ 40.05 40.26	40.45 40.34
Total "	72.59	72.34	72.89

ACTION OF CHLORINE UPON IODIDES OF PYRIDINE.

Pictet and Kraft[1] report several mixed perhalides of pyridine, quinoline, and piperidine. By adding iodine trichloride to a water solution of pyridine hydrochloride they get pyridine hydrochloride iodine chloride, $C_5H_5N.HCl.ICl$. Melting-point 180°. Analysis not given. The water present decomposes the iodine trichloride according to the equation,

$$2ICl_3 + 3H_2O = ICl + 5HCl + HIO_3.$$

By treating the above hydrochloride with caustic alkali, pyridine iodine chloride is formed, white needles melting at 132° C. Close analytical results are given. They report analogous products of quinoline and piperidine. The $C_5H_{11}N.HCl.ICl$, melting at 90° C. is of especial interest as it is made by adding iodine chloride (ICl) to piperidine hydrochloride and also by adding hydrochloric acid to piperidine iodine chloride, $C_5H_{11}N.ICl$.

Dittmar[2] uses iodine monochloride (ICl) and obtains the same bodies as reported by Pictet and Kraft. By chlorination of $C_5H_5N.HCl.ICl$ he obtains $C_5H_5N.HCl.ICl_3$. This is an unstable body and according to Pictet and Kraft cannot be made by treating the pyridine hydrochloride with iodine trichloride.

In our study we did not attempt to confirm the results just cited. Our aim was to study the effect of chlorine on pyridine derivatives containing iodine, hence we did not make use of iodides of chlorine direct.

Pyridine Hydriodide Trichloride, $C_5H_5N.HI.Cl_3$; or $C_5H_5N.HI.Cl_2$, $C_5H_5N.HI.Cl_4$; or $C_5H_5N.HCl.ICl$, $C_5H_5N.HCl.ICl_3$.—Chlorine gas was passed through a water solution of pure pyridine hydriodide to complete saturation. At first iodine is set free. It then combines with more chlorine and a bright lemon-yellow flocculent precipitate is formed. It crystallizes nicely from alcohol. Melting-point 176° C. The precipitate contains an abundance of iodine.

[1] *Bull. Soc. Chim.* [3], **7**. 72.
[2] *Ber. d. chem. Ges.*, **18**, 1613.

	Calculated for $C_5H_5N.HI.Cl_2$.	Found. I.	II.	III.
Titrated halogen	33.13	33.33	33.17	33.93
Total "	74.09	74.76	73.83	73.18

We could not by this method of simple chlorination obtain a body having four atoms of chlorine. The body we obtained consists probably of equal portions of the dichloride and tetrachloride.

Pyridine Methyl Iodide Tetrachloride, $C_5H_5N.CH_3I.Cl_4$, or $C_5H_5N.CH_3Cl.ICl_2$.—A canary-yellow powder melting at 185° C.

	Calculated for $C_5H_5N.CH_3I.Cl_4$.	Found.
Titrated halogen.....	39.17	39.16

Made by passing chlorine into a water solution of pyridine methyl iodide to saturation.

Bally[1] reports the same body, $C_5H_5N.CH_3Cl.ICl_2$, by passing chlorine into a mixture of $C_5H_5N.CH_3Cl.ICl$ and potassium hydroxide. He then acidifies and obtains a yellow body which melts at 179°–180° C. He makes $C_5H_5N.CH_3Cl.ICl$ by treating $C_5H_5N.CH_3I$ with chlorine. Melting-point 90° C.

Ostermayer[2] reports this last body, $C_5H_5N.CH_3Cl.ICl$, but with a melting-point of 81°–82° C., by treating $C_5H_5N.CH_3Cl$ with iodine chloride (ICl). The iodine chloride is made by passing chlorine into iodine suspended in water.

Pyridine Ethyl Iodide Tetrachloride, $C_5H_5N.C_2H_5I.Cl_4$, or $C_5H_5N.C_2H_5Cl.ICl_2$.—Made by passing chlorine through a water solution of pyridine ethyl iodide. At first iodine is thrown out of solution. Gradually the solution assumes a lighter color, the iodine disappears, and finally a canary-yellow precipitate is obtained. Melting-point 123° C.

	Calculated for $C_5H_5N.C_2H_5I.Cl_4$.	Found.
Titrated halogen.....	37.71	37.43
Total "	71.28	71.16

ACTION OF BROMINE UPON PYRIDINE.

Anderson[3] treats a water solution of pyridine with bromine water and reports (no analysis given) an addition product with probably more than one atom of bromine. He also treats dry

[1] *Ber. d. chem. Ges.*, **21**, 1772.
[2] *Ibid*, **18**, 591.
[3] *Ann. Chem.* (Liebig), **105**, 341.

pyridine with dry bromine and reports pyridine hydrobromide as one of the products formed (no analysis given).

Hofmann[1] treats pyridine hydrochloride with bromine and gets a body which he does not analyze but erroneously assumes to have the formula $C_5H_5N.Br_2$. More is given in this paper concerning this product under "Action of Bromine upon Chlorides of Pyridine."

Grimaux[2] treats pyridine with three times its volume of bromine and obtains an unstable body, which he crystallizes from chloroform or alcohol. He gets thin red plates, melting at 126° C., to which he assigns the formula $(C_5H_5NBr_2)_2HBr$. His analysis shows about two and one-half atoms of bromine to five atoms of carbon, but he does not report the action of reducing agents like sodium thiosulphate, which, if his formula be correct, would show four atoms of titrated bromine and five atoms of total bromine to ten atoms of carbon. We could not reproduce Grimaux's compound by this method. See further in this paper under "Action of Bromine upon Bromides of Pyridine."

After many ineffectual attempts to form a definite compound by the action of bromine in varying quantities upon dry pyridine and pyridine in water solution, pyridine was dissolved in a large excess of chloroform and treated with bromine vapors. A red oil separated at first which rapidly went into solution. As the solution became saturated with the bromine, fine dark red needle-like crystals separated out. These were carefully and rapidly dried and analyzed. Melting-point 58.5° C.

	Calculated for $C_5H_5N.Br_4$.	Calculated for $C_5H_5N.HBr.Br_3$.	Found. I.	Found. II.
Titrated bromine..	80.16	59.97	80.23 80.15	79.31
Total " ..	80.16	79.96	79.30 79.91	....

The tetrabromide is unstable and loses bromine upon exposure, becoming lighter in color. After several days it ceases to lose bromine and becomes light yellow with a melting-point of 94°–95° C. Titration gives 66.71 per cent. of bromine; theory for $C_5H_5N.Br_2$ gives 66.89 per cent. of bromine.

BROMIDES OF PYRIDINE.

Pyridine Hydrobromide, $C_5H_5N.HBr$.—Colorless transparent

[1] *Ber. d. chem. Ges.*, *1879*, 988.
[2] *Compt. rend.*, **95**, 85.

feathery scales, slightly deliquescent, soluble in alcohol, chloroform, and water, insoluble in ether, melts at 200° C. with decomposition. Made by neutralizing pure pyridine with hydrobromic acid and evaporating gently to crystallization.

	Calculated for $C_5H_5N.HBr$.	Found.
Bromine	49.93	49.17 49.93

Pyridine Methyl Bromide, $C_5H_5N.CH_3Br$, $\frac{1}{2}H_2O$.—Forms large translucent crystals from alcoholic solution, soluble in water, alcohol, and chloroform, insoluble in ether. Melts with slight decomposition at 135.5° C. Made by passing methyl bromide gas through pure pyridine cooled in salt and ice. The fine, white crystals were washed with ether and crystallized from alcohol.

	Calculated for $C_5H_5N.CH_3Br$, $\frac{1}{2}H_2O$.	Calculated for $C_5H_5N.CH_3Br$.	Found.
Bromine	43.88	45.33	44.23 43.72

We have not yet succeeded in preparing a sample that gives sufficient bromine for the pure bromide without some water of crystallization.

Pyridine Ethyl Bromide, $C_5H_5N.C_2H_5Br$.—White crystals melting at 111°–112° C., soluble in alcohol and water, insoluble in ether. Made by adding ethyl bromide to pure pyridine. At ordinary temperature the action is very slow and almost no heat is generated. When the mixture is warmed a violent action takes place with the generation of heat. An excess of ethyl bromide should be used and the flask provided with a reflux condenser. After the reaction has ceased (one-half hour) the ethyl bromide may be distilled off before crystallization from alcohol.

	Calculated for $C_5H_5N.C_2H_5Br$.	Found.
Bromine	42.49	41.82 41.88

ACTION OF IODINE UPON BROMIDES OF PYRIDINE.

Pyridine Hydriodide Periodide, $C_5H_5N.HI.I$.[1]—Iodine in alcoholic or potassium iodide solution displaces bromine in pyridine hydrobromide. The particular periodide formed depends upon temperature of experiment and amount of iodine used. When

[1] This Journal, 19, 327.

the crystals obtained are well washed with ether and recrystallized from alcohol, they are found to be entirely free from bromine. In this manner $C_5H_5N.HI.I$ was obtained and also higher periodides, which were only tested to prove the absence of bromine.

Pyridine Methyl Iodide Tetriodide, $C_5H_5N.CH_3I.I_4$.[1]—To an aqueous solution of pyridine methyl bromide a potassium iodide solution of iodine was added. Bronze-green crystals were formed at once. These, upon purification, showed entire absence of bromine and on analysis gave good figures for $C_5H_5N.CH_3I.I_4$. The same results were obtained using an alcoholic solution of iodine.

Pyridine Ethyl Iodide Periodide, $C_5H_5N.C_2H_5I.I_x$.—On treatment of pyridine ethyl bromide with alcoholic or with potassium iodide solution of iodine, an oil was obtained entirely free from bromine. This body could not be obtained in a crystalline condition. Analysis gives figures too high for the triiodide, $C_5H_5N.C_2H_5I.I_2$,[2] which melts at 51° C. This is probably the pentiodide, $C_5H_5N.C_2H_5I.I_4$, not entirely pure.

ACTION OF BROMINE UPON BROMIDES OF PYRIDINE.

Pyridine Hydrobromide Perbromide, $(C_5H_5N.HBr)_2Br_2$, or $C_5H_5N.HBr.Br, C_5H_5N.HBr.Br_2$.—Very stable, dark orange-colored prismatic crystals. Melting-point 125°C. Made by aspirating bromine through a water solution of pyridine hydrobromide until the orange crystals which first formed were dissolved in the excess of bromine. The oil was separated and became a crystalline solid upon exposure for the evaporation of the excess of bromine. This solid was heated on the water-bath for some time and then crystallized from alcohol.

	Theory for $(C_5H_5N.HBr)_2Br_2$.	Theory for $C_5H_5N.HBr.Br$.	Theory for $C_5H_5N.HBr.Br_2$.	Found.
Titrated bromine.	42.82	33.30	51.58	41.95
Total "	71.37	66.61	74.95	70.86

It is very probable that this is the same body reported by Grimaux[3] and referred to in this paper under "Action of Bromine upon Pyridine." However, he reports his product unstable, melting at 126° C. The body we obtain is perfectly stable, does

[1] This Journal, 19, 324.
[2] This Journal, 19, 329.
[3] *Compt. rend.*, 95, 85.

not give off bromine when heated on the water-bath and melts at 125° C. Grimaux assigns the formula $(C_5H_5NBr_2)_2HBr$, which differs from our formula in total amounts of the elements by one hydrogen atom, but differs widely in the structural relation. The total bromine and the combustion would give the same results for both formulas. Total bromine for Grimaux 71.50 per cent. According to his formula four atoms of the bromine are *per* halogen and should react with sodium thiosulphate, giving 57.38 per cent. of titrated bromine. Our formula calls for 42.85 per cent. of titrated bromine, which is confirmed by the analysis. This body is then a mixture of one molecule each of the mono- and dibromide of pyridine hydrobromide, and not the monohydrobromide of two molecules of pyridine dibromide.

By checking the bromination of the pyridine hydrobromide at the formation of the first crystals a lighter orange-colored body is obtained, which crystallizes nicely from alcohol and is perfectly stable. Melting-point 93° C.

	Calculated for $C_5H_5N.HBr.Br$.	Found.
Titrated bromine	33.30	32.66

Pyridine Methyl Bromide Dibromide, $C_5H_5N.CH_3Br.Br_2$.—A dark orange-red crystalline body. Melting-point 66° C. Soluble in alcohol and acetic ether, insoluble in carbon bisulphide, chloroform, water, and ether. It is decomposed by acetone. Made by aspirating bromine through a water solution of pyridine methyl bromide. The excess of bromine was driven off on the water-bath and the crystalline mass further purified by recrystallization from alcohol.

	Calculated for $C_5H_5N.CH_3Br.Br_2$.	Found. I.	Found. II.
Titrated bromine..	47.87	48.03	48.08
Total "	71.80	71.74	71.60

Ostermayer[1] treats pyridine methyl chloride with bromine and obtains a body melting at 48° C., which loses bromine in the air. He assigns the formula $C_5H_5N.CH_3Br.Br_2$, but reports no analysis.

Pyridine Ethyl Bromide Dibromide, $C_5H_5N.C_2H_5Br.Br_2$.—The same in appearance and properties as the methyl compound just

[1] *Ber. d. chem. Ges.*, 18, 599.

described, and made in the same manner. Melting-point 35° C.

	Calculated for $C_5H_5N.C_2H_5Br.Br_2$.	Found. I.	II.
Titrated bromine.....	45.94	45.55	45.35
Total "	68.91	68.90	68.40

ACTION OF CHLORINE UPON THE BROMIDES OF PYRIDINE.

Pyridine Hydrobromide Perchloride (?).—When chlorine is passed into a water solution of pyridine hydrobromide, some bromine is evolved and a reddish-yellow crystalline precipitate is formed. This precipitate becomes a yellow oil upon complete saturation with chlorine. Upon exposure or warming on the bath this becomes solid. Qualitative tests show an abundance of bromine and chlorine. The yellow crystals assume a reddish tinge when washed with water; this disappears if the crystals are then washed with ether. The compound is not stable; chlorine is evolved on standing, and possibly some bromine, although the bromine odor was not observed. This preparation was made several times, giving to all appearances exactly the same body, and having approximately the same melting-point, 51° C. Analysis, however, shows widely different results. It seems quite probable that $C_5H_5N.HCl.BrCl$ is formed, but in all cases impure, owing to the volatilization of some of the bromine as soon as it is set free by the chlorine and before it can enter into combination with more chlorine. Samples IV and V were given an extra long treatment with chlorine.

	Calculated for $C_5H_5N.HBr.Cl$.	Calculated for $C_5H_5N.HCl.BrCl$.	Found. I.	II.	III.	IV.	V.
Titrated halogen	18.17	30.68	25.59	15.63	13.48	16.93	16.85
			25.28	14.72	13.30	16.75	16.62
			24.16	14.79	13.62	....	....
			25.12	....	13.22	....	....
			23.60	....	11.90	....	....
			23.29	....	....	....	....
Total "	59.01	65.29	57.30	....	53.04	65.02	63.69
			57.46		54.89	65.82	62.41

Pyridine Methyl Bromide Dichloride, $C_5H_5N.CH_3Br.Cl_2$, or $C_5H_5N.CH_3Cl.BrCl$.—When pyridine methyl bromide in water solution is treated with chlorine some bromine escapes and a light yellow precipitate forms, becoming a red oil upon complete saturation with chlorine. This body is not stable, but upon standing or gently warming loses most of its halogen odor and becomes solid at about 19° C.

	Calculated for $C_5H_5N.CH_3Br.Cl_2$.	Calculated for $C_5H_5N.CH_3Br.Cl$.	Found. I.	Found. II.
Titrated halogen..	29.00	16.90	{ 27.96 { 27.86	27.94 27.85
Total " ..	61.56	55.06	61.00	61.12

Pyridine Ethyl Bromide Dichloride, $C_5H_5N.C_2H_5Br.Cl_2$, or $C_5H_5N.C_2H_5Cl.BrCl$.—A pale yellow precipitate is first formed, when chlorine is passed into a water solution of pyridine ethyl bromide. Some bromine escapes. This precipitate becomes a red oil upon complete saturation with chlorine. This oil could not be purified so as to obtain a crystalline body. The oil was gently warmed for some time and analyzed.

	Calculated for $C_5H_5N.C_2H_5Br.Cl_2$.	Calculated for $C_5H_5N\ C_2H_5Br.Cl$.	Found. I.	Found. II.
Titrated halogen..	27.43	15.84	{ 27.19 { 26.13	27.77 27.81
Total " ..	57.49	51.60	55.15	55.75

ACTION OF CHLORINE UPON PYRIDINE.

Anderson[1] treats pyridine with chlorine and gets pyridine hydrochloride and a white product having the hypochlorite odor. No analysis reported.

Kaiser[2] treats pure pyridine with dry chlorine and obtains ultimately a hydrochloride of dichlorpyridine, $C_5H_3Cl_2N.HCl$, a substituted body and pyridine chloride, $C_5H_5N.Cl$, an addition body. He also treats pyridine dissolved in water with chlorine gas and obtains an addition-product having a chloride of lime odor. He concludes that this is pyridine hypochlorite, $C_5H_5N.HOCl$. Upon passing more chlorine into this product pyridine is decomposed with evolution of carbon dioxide, nitrogen, etc. When he treats pyridine and potassium hydroxide with chlorine, chloroform, dichloracetic acid, carbon dioxide, and nitrogen are formed.

We treated a chloroform solution of pyridine with dry chlorine to complete saturation. A few oily drops formed at the first which almost immediately went into solution, and no further change was noticed during the long-continued chlorination. The solution was then gently evaporated to expel the excess of chlorine and the chloroform. A brownish colored oil was left behind which did not solidify upon standing. On addition of a

[1] *Ann. Chem.* (Liebig), 105, 340.
[2] *Am. Chem. J.*, 8, 312.

few drops of water the oil becomes a white flocculent powder, which does not dissolve in great excess of water. This oil has an odor somewhat like chloride of lime. When a crystal of potassium iodide is added to the oil no iodine is set free, nor when to this water and hydrochloric acid are added. Iodine is not set free when potassium iodide is added to the oil after the addition of water. This seems to be conclusive proof that the body is not a hypochlorite or a perchloride of pyridine. We hope later to investigate this body more fully.

CHLORIDES OF PYRIDINE.

Pyridine Hydrochloride, $C_5H_5N.HCl$.—Transparent, colorless crystals, soluble in alcohol, chloroform, hydrochloric acid, and water; insoluble in ether, and is thrown down from its alcoholic solution by the addition of ether. It crystallizes in scales from a solution in absolute alcohol. It cannot be crystallized from its water solution. It is made by adding concentrated hydrochloric acid in excess to pure pyridine. The solution is heated on the bath and then cooled over sulphuric acid. The salt separates out as a mass of thin scales, which are purified by recrystallization from absolute alcohol. Melting-point 82° C.[1]

	Calculated for $C_5H_5N.HCl$.	Found.
Chlorine.....	30.73	{ 30.23 { 30.28

Pyridine Methyl Chloride, $C_5H_5N.CH_3Cl$.—Ostermayer[2] has reported the formation of this salt by heating pyridine, hydrochloric acid, and methyl alcohol to 230° C. for ten hours. He fails to obtain stable crystals but proves the purity of his syrupy solution by the formation and analysis of the gold and platinum double salts.

Lange[3] makes the pyridine methyl chloride by shaking the iodide with moist silver chloride. We tried to obtain the chloride in crystalline form by saturating pure pyridine with methyl chloride; failing in this we adopted the method of Lange. This

[1] The sample from which the melting-point was obtained was made by passing dry hydrochloric acid gas into dry pyridine cooled in ice. This was well washed with ether, and melting-point taken. This preparation distils with some decomposition. A strong odor of pyridine is observed. Voluminous white vapors are formed, which condense on the sides of the flask and thermometer, and solidify when cooled to 118° C.

[2] *Ber. d. chem. Ges.*, **18**, 591.

[3] *Ibid*, *1885*, 3438.

same method was used in the preparation of pyridine ethyl chloride. Whenever the pyridine methyl or ethyl chloride was desired the corresponding iodide was shaken with an excess of freshly precipitated silver chloride, till a portion of the clear liquid gave no test for iodine. The chloride was always used in solution. All attempts to obtain the crystalline body failed.

ACTION OF IODINE UPON CHLORIDES OF PYRIDINE.

Pyridine Hydriodide Hexiodide, $C_5H_5N.HI.I_6$.[1]—When an alcoholic solution of iodine is added to pyridine hydrochloride, the latter being in excess, a dark crystalline body is obtained which, when crystallized from alcohol, gives tests for chlorine. When an excess of alcoholic solution of iodine is added to pyridine hydrochloride the heptiodide, $C_5H_5N.HI.I_6$, fairly pure, is obtained perfectly free from chlorine after a second crystallization from alcohol. Melting-point 71°–72° C.

Pyridine Methyl Iodide Tetriodide,[2] $C_5H_5N.CH_3I.I_4$.—When an excess of alcoholic solution of iodine is added to pyridine methyl chloride, a dark green oil is at once formed. This is carefully separated and dissolved in alcohol. From this solution, after a second treatment with alcohol, fine needle-like crystals are obtained free from chlorine. Analysis shows these crystals to be the pentiodide.

Pyridine Ethyl Iodide Periodide, $C_5H_5N.C_2H_5I.I_2$.—When an alcoholic solution of iodine, in excess, is added to pyridine ethyl chloride, a dark green oil is formed. This is carefully separated and dissolved in alcohol and is again obtained as an oil which does not contain chlorine. All attempts to obtain a crystalline body failed, and analysis of the oil showed it to be an impure periodide, but containing more iodine than required for $C_5H_5N.C_2H_5I.I_2$, which melts at 51° C.[3]

ACTION OF BROMINE UPON CHLORIDES OF PYRIDINE.

Pyridine Hydrobromide Dibromide, $C_5H_5N.HBr.Br_2$, $2H_2O$.—Pure pyridine was treated with an excess of dilute hydrochloric acid and then saturated with bromine. A bromine-colored oil is formed, which becomes solid upon exposure and loses its bro-

[1] This Journal, 19, 328.
[2] This Journal, 17, 859.
[3] This Journal, 19, 329.

mine odor upon warming. The crude product melts at 94° C., and that crystallized from alcohol at 118°–120° C. The crystals are orange-yellow. In sample I, the crude product was well washed with chloroform but not crystallized, II is the crude product, III is the crude product washed with chloroform and then crystallized from alcohol. I and II do not contain even a trace of chlorine. When dissolved in absolute alcohol and placed in a freezing mixture, the crystals form as prismatic bars very sharply defined.

	Calculated for $C_5H_5N.HBr.Br_2, 2H_2O$.	Calculated for $C_5H_5N.HBr.Br$.	Found. I.	II.	III.
Titrated bromine	44.59	33.30	44.33 44.08	43.74 43.20	44.24 44.23
Total "	67.36	66.61	67.55 66.51	66.38 66.01	67.96 ....

Pyridine Hydrobromide Perbromide, $C_5H_5N.HBr.Br$.—Pure pyridine hydrochloride was dissolved in chloroform and brominated. Stellate masses of flat golden needles were obtained. These were dried and crystallized from alcohol. Free from chlorine. Melting-point 88° C.

	Calculated for $C_5H_5N.HBr.Br$.	Found.
Titrated bromine	33.30	33.18 33.39
Total "	66.61	66.66 66.82

Pyridine Methyl Bromide Perbromide, $C_5H_5N.CH_3Br.Br$.—Ostermayer[1] treats pyridine methyl chloride with bromine and obtains $C_5H_5N.CH_3Br.Br_2$, melting-point 48° C. Loses bromine in the air. Great difficulty was experienced in confirming Ostermayer's work. In one experiment a yellow compound was obtained free from chlorine, melting at 82°–83° C., which gave fairly good results for $C_5H_5N.CH_3Br.Br$.

	Calculated for $C_5H_5N.CH_3Br.Br$.	Found.
Titrated bromine	31.46	32.09
Total "	62.93	64.41

Pyridine Methyl Bromide Dibromide, $C_5H_5N.CH_3Br.Br_2$.—Most of the experiments gave results indicating a compound between the dibromide and the tribromide. Finally, after several hours bromination, a product was obtained which crystallized from

[1] *Ber. d. chem. Ges.*, 18, 599.

absolute alcohol in orange-colored needles and was entirely free from chlorine. Melting-point 55° C., not 48° C. as reported by Ostermayer. We brominated $C_5H_5N.CH_3Br$ and get $C_5H_5N.CH_3Br.Br_2$. Melting-point 66° C.

	Calculated for $C_5H_5N.C_2H_5Br.Br_2$.	Found.
Titrated bromine	47.87	{ 46.29 { 46.47
Total "	71.80	{ 71.59 { 70.97

Pyridine Ethyl Bromide Dibromide, $C_5H_5N.C_2H_5Br.Br_2$, $2H_2O$. —Bromine vapors were passed through a water solution of pyridine ethyl chloride. A dark red oil was obtained which was warmed on the water-bath to remove excess of bromine. This oil would not solidify in a freezing mixture until a small piece of ice was added, when it became a mass of thin, reddish brown laminae, melting at 15° C., and solidifying at once when cooled below that temperature. This body was dissolved in absolute alcohol, using very gentle heat. It is decomposed by hot alcohol. Again, upon cooling, crystals could not be obtained until a small piece of ice was added, when it solidified as before. Melting-point 15° C. A qualitative test shows entire absence of chlorine.

	Calculated for $C_5H_5N.C_2H_5Br.Br_2$, $2H_2O$.	Found.
Titrated bromine	41.62	41.65
Total "	62.44	62.61

ACTION OF CHLORINE UPON CHLORIDES OF PYRIDINE.

The effect of chlorine was studied upon the hydrochloride, methyl chloride, and ethyl chloride of pyridine in water solution. No perchloride is formed, for upon heating on the water-bath to remove the excess of chlorine the solutions do not liberate iodine from a potassium iodide solution.

Molecular Weight Determinations.—The cryoscopic method was used with a number of the above-described mixed perhalides, using phenol as a solvent. In most cases the results were not close but all plainly indicated the monopyridine molecule as the probable structure.

SUMMARY.

The range of formation with the periodides is great, C_5H_5N.

HI.I to $C_5H_5N.HI.I_6$, with the perbromides slight, and zero with the perchlorides. With the normal perhalides, increase in halogen lowers the melting-point. With the normal halide the hydrogen halide melts highest, the methyl halide lower, and the ethyl halide lowest.

In the mixed perhalides the power of displacement and the position of the halogen atoms in the molecule are points of great interest. Iodine in excess displaces bromine and chlorine completely, forming periodides from the normal bromides and chlorides. Bromine seems to displace iodine from the pyridine normal iodides and then combines with it to form a bromoiodide of a normal bromide. Bromine displaces chlorine completely, forming perbromides from the normal chlorides. Chlorine seems to displace both iodine and bromine at first to form normal chlorides, then it combines with the displaced halogen (some of the bromine always escapes) to form mixed perhalides, ICl, ICl_3, BrCl, $BrCl_3$, of the normal chlorides, *e. g.*, $C_5H_5N.HCl.ICl_3$ from $C_5H_5N.HI$ and Cl_2. The mixed perhalides containing bromine and iodine show color reaction for iodine when treated with carbon bisulphide, indicating that the iodine is probably present as *per*iodine. Also the mixed perhalides containing bromine and chlorine show color tests for bromine, indicating that the bromine is *per*bromine. When an alcoholic solution of the perhalide containing bromine and iodine is titrated with sodium thiosulphate, evaporated to dryness, and the organic body thoroughly extracted; both bromine and iodine are found in the residue of sodium salts. In the following summary, unless references are given, the description of the preparations and needed references are found in the body of this paper:

1. *Action of Iodine upon Pyridine.*[1]
   $C_5H_5N.I_4$. Greenish black. Melting-point 85° C.
2. *Action of Bromine upon Pyridine.*
   $C_5H_5N.Br_2$. (?) Hofmann.
   $(C_5H_5N.Br_7)_2HBr$. (?) Grimaux.
   $C_5H_5N.Br_4$. Dark red. Melting-point 58.5° C.
   $C_5H_5N.Br_2$. Light yellow. Melting-point 94°–95° C.
3. *Action of Chlorine upon Pyridine.*
   $C_5H_5N.HCl$. Anderson.
   $C_5H_3Cl_2N.HCl$. Kaiser.

[1] This Journal, 17, 865.

$C_5H_5N.Cl$. (?) Kaiser.
$C_5H_5N.HOCl$. (?) Kaiser.

4. *Iodides of Pyridine.*

$C_5H_5N.HI$. Colorless. Melting-point 268° C.[1]
$C_5H_5N.CH_3I$. Colorless. Melting-point 117° C.[2]
$C_5H_5N.C_2H_5I$. Colorless. Melting-point 90.5° C.[3]
$C_5H_5N.C_3H_7I$. Baer. Colorless. Melting-point 52°–53° C.[4]
$C_5H_5N.C_3H_7I$(iso). Baer. Colorless. Melting-point 114°–115° C.[5]

5. *Bromides of Pyridine.*

$C_5H_5N.HBr$. Colorless. Melting-point 200° C.
$C_5H_5N.CH_3Br$, $\frac{1}{2}H_2O$. Colorless. Melting-point 135.5° C.
$C_5H_5N.C_2H_5Br$. Colorless. Melting-point 111°–112° C.

6. *Chlorides of Pyridine.*

$C_5H_5N.HCl$. Colorless. Melting-point 82° C.
$C_5H_5N.CH_3Cl$. Ostermayer, Lange. Not obtained in crystals.
$C_5H_5N.C_2H_5Cl$. Not obtained in crystals.

7. *Action of Iodine upon the Iodides of Pyridine.*

$C_5H_5N.HI.I$. Dark brown. Melting-point 188°–192° C.[6]
$C_5H_5N.HI.I_2$. Has not been prepared.
$C_5H_5N.HI.I_3$. This and the $I.I_5$ probably do not exist.
$C_5H_5N.HI.I_4$. Brownish black. Melting-point 78°–85° C.[7]
$C_5H_5N.HI.I_6$. Lustrous green scales. Melting-point 63°–64° C.[8]
$C_5H_5N.CH_3I.I$. Reddish brown. Melting-point 91.5° C.[9]
$C_5H_5N.CH_3I.I_2$. Dark red. Melting-point 50° C.[10]
$C_5H_5N.CH_3I.I_3$. This and the $I.I_5$ probably do not exist.
$C_5H_5N.CH_3I.I_4$. Greenish black. Melting-point 47.5° C.[11]
$C_5H_5N.CH_3I.I_6$. Green. Melting-point 26° C.[12]
$C_5H_5N.C_2H_5I.I$. Has not been prepared.
$C_5H_5N.C_2H_5I.I_2$. Bluish black. Melting-point 51° C.[13]
$C_5H_5N.C_2H_5I.I_4$. (?) Black. Melting-point 83° C.[14]
$C_5H_5N.C_2H_5I.I_6$. Has not been made.

8. *Action of Bromine upon the Iodides of Pyridine.*

$C_5H_5N.HBr.IBr$. Reddish brown. Melting-point 172°–175° C.
$C_5H_5N.CH_3Br.IBr$. Orange yellow. Melting-point 61°–62° C.
$C_5H_5N.C_2H_5Br.IBr$. Orange yellow. Melting-point 25°–26° C.

9. *Action of Chlorine upon the Iodides of Pyridine.*

$C_5H_5N.HCl.ICl$. Melting-point 180° C. Pictet and Kraft, Dittmar.
$C_5H_5N.ICl$. White needles. Melting-point 132° C. Pictet and Kraft.

[1] This Journal, 19, 327.
[2] This Journal, 18, 91.
[3] This Journal, 18, 92.
[4] This Journal, 18, 92.
[5] This Journal, 18, 93.
[6] This Journal, 19, 327.
[7] This Journal, 17, 867, and 19, 328.
[8] This Journal, 19, 328.
[9] This Journal, 17, 860.
[10] This Journal, 17, 860.
[11] This Journal, 19, 322.
[12] This Journal, 19, 323.
[13] This Journal, 19, 329.
[14] This Journal, 19, 32.

$C_5H_5N.HCl.ICl_3$. Dittmar.

$C_5H_5N.HCl.ICl$, $C_5H_5N.HCl.ICl_3$. Lemon yellow. Melting-point 176° C.

$C_5H_5N.CH_3Cl.ICl_3$. Canary yellow. Melting-point 185° C.

$C_5H_5N.CH_3Cl.ICl_3$. Yellow. Bally. Melting-point 179°–180° C.

$C_5H_5N.CH_3Cl.ICl$. Bally. Melting-point 90° C.

$C_5H_5N.CH_3Cl.ICl$. Ostermayer. Melting-point 81°–82° C.

$C_5H_5N.C_2H_5Cl.ICl_3$. Canary yellow. Melting-point 123° C.

10. *Action of Iodine upon the Bromides of Pyridine.*

$C_5H_5N.HI.I$, and higher periodides.

$C_5H_5N.CH_3I.I_4$.

$C_5H_5N.C_2H_5I.Ix$.

11. *Action of Bromine upon the Bromides of Pyridine.*

$C_5H_5N.HBr.Br$, $C_5H_5N.HBr.Br_2$. Dark orange. Melting-point 125° C.

$(C_5H_5N.Br_2)_2HBr$. (?) Grimaux. Melting-point 126° C.

$C_5H_5N.HBr.Br$. Light orange. Melting-point 93° C.

$C_5H_5N.CH_3Br.Br_2$. Dark orange-red. Melting-point 66° C.

$C_5H_5N.CH_3Br.Br_2$. Ostermayer. Melting-point 48° C.

$C_5H_5N.C_2H_5Br.Br_2$. Dark orange-red. Melting-point 35° C.

12. *Action of Chlorine upon the Bromides of Pyridine.*

$C_5H_5N.HCl.BrCl$. (?) Yellow. Melting-point 51° C.

$C_5H_5N.CH_3Cl.BrCl$. Yellow. Melting-point 19° C.

$C_5H_5N.C_2H_5Cl.BrCl$. Red oil.

13. *Action of Iodine upon the Chlorides of Pyridine.*

$C_5H_5N.HI.I_6$.

$C_5H_5N.CH_3I.I_4$.

$C_5H_5N.C_2H_5I.Ix$.

14. *Action of Bromine upon the Chlorides of Pyridine.*

$C_5H_5N.HBr.Br_2$, $2H_2O$. Orange-yellow. Melting-point 118°–120° C.

$C_5H_5N.HBr.Br$. Golden yellow. Melting-point 88° C.

$C_5H_5N.CH_3Br.Br$. Ostermayer. Melting-point 48° C.

$C_5H_5N.CH_3Br.Br$. Yellow. Melting-point 82°–83° C.

$C_5H_5N.CH_3Br.Br_2$. Orange. Melting-point 55° C.

$C_5H_5N.C_2H_5Br.Br_2$, $2H_2O$. Reddish brown. Melting-point 15° C.

15. *Action of Chlorine upon the Chlorides of Pyridine.*

No perchlorides formed. (See body of paper.)

We wish to express our thanks to Professor A. B. Prescott, in whose laboratory and under whose general supervision the work has progressed. A paper on "Perhalides of Quinoline" is nearly ready, and work is continued upon "Halogen Derivatives of the Alkaloids with a View to Methods of Analysis."

ANN ARBOR, MICH., May 19, 1897.

A MODIFICATION OF THE PERMANGANATE METHOD FOR THE DETERMINATION OF IRON.

By Hamilton P. Cady and Alfred P. Ruediger.

Received April 30, 1897.

THE methods generally employed for the volumetric determination of iron, are the permanganate and Kessler's modification of the bichromate method. The general accuracy of these methods cannot be doubted and the only objection to them is the time that they consume. If potassium bichromate be used the titration may be made in the presence of hydrochloric acid, and stannous chloride can be employed as a reducing agent. The actual process of titration however is very tedious and in many cases is not as accurate as determinations by the permanganate method.

In using the old permanganate method, however, the solutions must be free from hydrochloric acid as potassium permanganate is decomposed by the acid in the presence of ferric salts. On this account the hydrochloric acid is usually driven off by evaporation with sulphuric acid, and the iron is afterwards reduced by zinc. This is at best a long and tedious process. If the hydrochloric acid is not driven off, the action of ferric salts must be prevented by the addition of some substance. The ferric salts seem to act catalytically,[1] for oxalic acid may be titrated in hydrochloric acid solution with potassium permanganate with perfect sharpness, and without a trace of chlorine being set free, showing that the decomposition of the permanganate is not due to the hydrochloric acid alone.

The catalytic action of the ferric salts may be very much diminished by the addition of other salts such as the sulphates of magnesium, zinc, and manganese, and several methods have been devised in which advantage is taken of this property of these salts. The use of manganous sulphate for this purpose was first proposed by C. Zimmerman[2]. He gives a number of analyses showing the agreement between the results obtained from the hydrochloric and the sulphuric acid solutions. Zinc was used as the reducing agent.

Reinhart[3] improved Zimmerman's method by using stannous

[1] Ostwald's Foundations of Analytical Chemistry, p. 144.

[2] *Ber. d. chem. Ges., 1884*, **15**, 779.

[3] *Stahl und Eisen*, **4**, 704.

chloride as a reducing agent, removing any excess of the latter with mercuric chloride and adding sulphuric and phosphoric acids to the manganous sulphate solution. The addition of the phosphoric acid permits the formation of ferric phosphate, a solution of which is nearly colorless, and does not obscure the end-reaction as the yellow ferric chloride would otherwise do.

C. T. Mixer and H. W. DuBois[1] modified this method slightly and gave a number of analyses showing the close agreement between the results obtained by this and by other methods.

The electric conductivity of solutions of the mercuric halides shows that they are ionized to an extremely slight extent, while the mercuric salts of oxygen acids are dissociated normally.

Since compounds of slight ionization always result when their constituent ions meet, mercuric halides are invariably formed when a mercuric salt of an oxygen acid is added to a solution containing halogen ions. If an excess of the salts of the oxygen acid be added the presence of the mercury ions derived from its dissociation, will diminish the already very slight ionization of the mercuric halogen compound, until it is practically nothing. Hence the solution would contain no halogen ions. As is well known there must be dissociation or the formation of ions before a chemical reaction can take place, and under the conditions above mentioned there will be no formation of halogen ions, hence such a solution will show none of the characteristic reactions of the halogens.

As an illustration of the foregoing, it may be noted that silver nitrate will give no precipitate in a dilute solution of a chloride in the presence of an excess of mercuric sulphate, and also that silver chloride is moderately soluble in a solution of mercuric sulphate.

From these general principles we concluded that it ought to be possible to titrate iron with permanganate in the presence of hydrochloric acid if an excess of mercuric sulphate be added to the solution. A number of experiments to test this conclusion were then made, with very satisfactory results.

In order to compare the results obtained in hydrochloric and in sulphuric acid solutions the following experiments were tried:

[1] This Journal, 17, 405.

Five grams of ammonium ferrous sulphate dissolved in 500 cc. of water and 100 cc. of this solution were used for each titration.

		Per cent. of iron. Found.	Theory.
No. 1.	Sulphuric acid alone	14.21	14.28
No. 2.	" " "	14.21	14.28
No. 3.	" " "	14.28	14.28
No. 4.	Sulphuric acid with 5 cc. hydrochloric acid, and mercuric sulphate	14.21	14.28
No. 5.	Sulphuric acid with ten cc. of hydrochloric acid and mercuric sulphate	14.28	14.28

In order to determine whether this process would be applicable where stannous chloride was used as a reducing agent, a number of tests were made upon ammonium ferric alum, and in these determinations and for all subsequent analyses the following solutions were employed.

Solution A.—A five per cent. solution of stannous chloride. This solution need not necessarily be freshly prepared, but a portion of it should give no precipitate when diluted with twenty times its volume of water and boiled. The solution may be kept in good condition by acidifying with hydrochloric acid and putting a few fragments of tin into the bottle.

Solution B.—Hydrochloric acid, of a specific gravity 1.10, made by mixing equal volumes of acid of specific gravity 1.20 and water.

Solution C.—A mercuric sulphate solution. This is made by adding to 200 grams of mercuric sulphate eighty cc. of sulphuric acid (conc.) and adding this paste to 800 cc. of water. (If a yellow precipitate of basic mercuric sulphate is formed add more sulphuric acid.) To this is added 100 grams of orthophosphoric acid, dissolved in a little water and the whole is diluted to one liter.

If a good quality of mercuric sulphate is not at hand the salt may be easily prepared by heating metallic mercury in a porcelain evaporating dish on a sand-bath, with one and a half times its weight of concentrated sulphuric acid, as long as fumes of sulphuric acid are given off or till a sample of the salt does not become moist on exposure to the air. The mercuric sulphate should be tested by dissolving a portion of it in water, acidulated with sulphuric acid, and adding hydrochloric acid. If a

precipitate is produced the salt must be reheated with sulphuric acid.

METHOD I.

A process of analysis that we have found to be convenient is to dissolve the substance in water with a varying quantity of hydrochloric acid and heat to boiling after diluting to 100 cc., reducing with stannous chloride, adding small portions at a time until the solution becomes colorless, and a droplet gives no coloration with potassium thiocyanate. In order to oxidize any excess of stannous chloride that may have been used, a solution of potassium permanganate is added drop by drop until a droplet of the iron solution gives a faint but distinct color with potassium thiocyanate; stannous chloride, not more than one or two drops, is then added very cautiously. This whole process should be carried on at a boiling heat. The solution is then cooled and fifty cc. of dilute sulphuric acid is added, and for every ten cc. of hydrochloric acid that has been used, add thirty-five cc. of the mercuric sulphate solution, dilute to 400 cc., and titrate with potassium permanganate as usual. If the process of reduction has been properly carried out there will be only a slight precipitate of mercurous chloride formed from the reducing action of the stannous chloride, but if any great excess of stannous chloride has been added a heavy white precipitate will result and in such cases the determination cannot be relied upon.

METHOD II.

The substance is dissolved, best in a small Erlenmeyer flask in fifteen cc. of hydrochloric acid (solution B), two cc. of mercuric sulphate (solution C) is added, the whole is heated to boiling, and stannous chloride is added in small quantities at a time. The precipitate that may be temporarily produced as each drop of the stannous chloride is added, will dissolve after boiling a few seconds, until all the iron is reduced, when the solution becomes colorless, and the addition of a single drop of stannous chloride produces a perceptible turbidity or a precipitate, which does not redissolve on boiling. This shows the end of the reduction. The contents of the flask is rinsed into a beaker and diluted to about 300 cc., fifty cc. of dilute sulphuric acid are added, and then forty-five cc. of the mercuric sulphate (solution

C). The solution is then ready for titration without cooling as the amount added should cool it sufficiently.

Method I can be used in all cases, while Method II (which is much shorter), can always be used where there is not too much insoluble residue, which might obscure the reaction at the end of the reduction.

ANALYSIS OF AMMONIUM FERRIC ALUM BY METHOD I.

	Per cent. of iron found.	Oxygen =15.8, theory.
No. 1.	11.64	11.62
No. 2.	11.66	....
No. 3.	11.68	....
No. 4.	11.61	....
Average of 10 others	11.67	....

ANALYSIS OF AMMONIUM FERRIC ALUM BY METHOD II.

No. 1.	11.74	....
No. 2.	11.74	....
By reduction with zinc in a sulphuric acid solution.		
No. 1.	11.74	....
No. 2.	11.74	....

The results obtained by Method II would naturally be higher than those by Method I on account of the removal of a little iron in the process of testing in the latter case.

APPLICATION OF THE PROCESS TO IRON ORES.

In the analysis of ores, if the material be soluble in hydrochloric acid, it is boiled for some time with ten to fifteen cc. of solution B, until completely decomposed. The addition of some of the stannous chloride solution to the hydrochloric acid hastens the process of decomposition. When the ore is completely decomposed, if Method I is to be followed, the solution is diluted to 100 cc. and reduced as described under the above head. If Method II is to be followed, which is usually the better, the solution is not diluted but the two cc. of mercuric sulphate is added at once and the process continued as described. If long boiling was required for the decomposition of the ore, the greater part of the hydrochloric acid may have been driven off. Under these conditions the precipitate formed by the addition of a small quantity of stannous chloride will not readily redissolve, even when considerable ferric salts remained in the solution. In

such a case a few more cubic centimeters of hydrochloric acid should be added. Ores not soluble in hydrochloric acid may be dissolved after fusion with potassium hydrogen sulphate and then reduced by either method.

RESULTS.

Name.	Iron found. Per cent.
Limonite, No. 1	35.08
" "	35.02
Limonite, No. 2	54.37
" "	54.49
" "	54.49
Limonite, No. 3	37.47
" "	37.43
Limonite, No. 4	36.68
" "	36.68
" "	36.72
Magnetite,	71.87
"	71.64
"	71.64
"	71.87

In the analysis of the magnetite the determination was made upon a small quantity of the ore, three-tenths gram in each case, so any slight error in reading the burette was increased. The analyses of the limonites Nos. 3 and 4 were made by two different persons independently, and in each case they were entirely unfamiliar with the process, and good results were obtained without practice. This shows these modifications are easily mastered, and not difficult of execution.

The solution of mercuric sulphate described above contained one gram of the salt in five cc., and since four grams of mercuric sulphate are required to completely non-ionize one gram of hydrochloric acid, it is evident that thirty-five cc. of the mercuric sulphate solution will not be sufficient for all the chlorine in ten cc. of hydrochloric acid (sp. gr. 1.10); but much of the hydrochloric acid will escape during the process of dissolving the ore, and experience has shown us that thirty-five cc. of the mercuric sulphate solution is sufficient to combine with the chlorine that is left.

If too little mercuric sulphate has been added, the solution will smell of chlorine after the addition of permanganate. On the other hand a very great excess of mercuric sulphate will lower

the ionization of the mercuric chloride until it becomes lower than that of the mercurous chloride (formed by the reducing action of stannous chloride), and then the latter will dissolve, forming mercuric chloride and mercurous sulphate. Since mercurous sulphate exerts a reducing action on permanganate, this will introduce an error into the determination. Our experiments have shown that anywhere from twenty-five to fifty cc. of mercuric sulphate solution to ten cc. of hydrochloric acid, will give accurate results in the presence of small quantities of mercurous chloride.

The points requiring special care in this process then are:

1. Use stannous chloride that is in good condition.

2. Have the smallest possible excess of stannous chloride present after the reduction is completed.

3. Carefully adjust the proportions between the mercuric sulphate and the hydrochloric acid.

The speed of this process leaves nothing to be desired. Less than three minutes, in the case of soluble salts, has been found sufficient time for solution, reduction, and titration.

In conclusion we wish to acknowledge our indebtedness to Prof. E. H. S. Bailey for his advice and many valuable suggestions during the progress of the work.

A NEW APPARATUS FOR SULPHUR DETERMINATIONS IN IRON AND STEEL AND A USEFUL FORM OF WASH-BOTTLE.

By Richard K. Meade.

Received April 26, 1897.

THE writer has found the two forms of chemical apparatus mentioned below of much use in his work and describes them here, in the hope that they may prove of equal service to other analysts. The first description is that of an apparatus to be used in the determination of sulphur in iron and steel, by the method of conversion into hydrogen sulphide and absorption of the evolved gas, in an alkaline solution of lead nitrate.

The apparatus is shown, drawn to one-eighth scale, in Fig. 1. It consists of the following parts:

1. A half liter flask, of the "Joliet" pattern, such as is used in the laboratories of iron and steel companies. The flask is

fitted with a rubber stopper, having two holes, through one of which passes a funnel with glass stop-cock, and through the other a piece of glass tubing, bent at right angles about its middle point.

2. A one-ounce separatory funnel, cylindrical in shape, fitted with a two hole rubber stopper, provided with tubes for the admission and exit of the gases, as shown in the cut. The

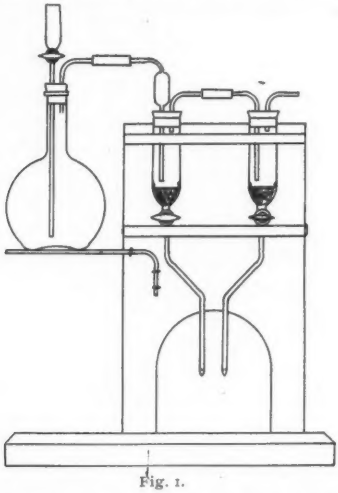


Fig. 1.

delivery tube is blown into a bulb of twenty-five to fifty cc. capacity, in order to prevent any of the solution in the funnel from being sucked into the evolution flask. The funnel itself is dented in three places, the same distance and about one-half inch from the bottom of the funnel, or just where the walls begin to narrow to meet the stop-cock. This may be easily done by cautiously heating the funnel in the flame of a blast-lamp and then pressing lightly at the desired points of indentation, with an iron wire. In the bottom of the funnel is placed a little glass wool, and upon this sufficient asbestos to reach even with the dents in the walls of the funnel. Over this a thin perforated disk of platinum, made to fit the funnel closely, is pressed down under the dents, holding the asbestos in place. The stems of the funnels are bent as shown in the sketch.

3. A separatory funnel, fitted similarly to the one described above, except that the tube leading into it need not be blown into a bulb.

4. A wooden base or stand upon which the whole rests. It is made exactly as shown in the sketch. The guide or upper cross piece is one and three-fourths inches wide and made solid. The rest, or lower one, is the same width, but is split along its middle, hinged at one end and fastened at the other by a catch, to allow the removal of the funnels when desirable. The iron ring, upon which the flask rests, is forged of one-fourth inch wrought iron and is fastened to the stand by means of staples.

The solution of the drillings, the preparation of the absorbent solution, and the precipitation of the sulphur as barium sulphate is conducted according to Blair, as described in his admirable book, "The Chemical Analysis of Iron."

The separatory funnels are half filled with an alkaline solution of lead nitrate, the sample weighed into the flask, the apparatus connected together and dilute acid poured upon the drillings. When action slackens, a lamp is placed under the flask and its contents boiled until all gas is given off. Pass a moderately rapid current of hydrogen through the apparatus for a few minutes and then disconnect the flask and funnels. Open the stop-cocks to the separatory funnels and allow the alkaline solution to run into a beaker, previously placed under them. The lead sulphide is caught by and retained upon the filters. Wash off the tubes into the funnels and pass a stream of water, from a wash-bottle, around the sides of the funnels several times, allowing the wash water to run through the filter into the beaker. Close the stop-cocks, remove the beaker under the funnels and put a clean one in its place. Drop a little powdered potassium chlorate, free from sulphur, into the funnels, and then add ten to twenty cc. of concentrated hydrochloric acid. Stand the apparatus in a hood, or where the fumes will be carried off readily, and open the stop-cocks of the funnels, allowing the acid to drop slowly into the beaker. As it passes through the filters it dissolves any sulphide which may be mixed with the asbestos. Wash the funnels and filters well with water, allowing the washings to run into the beaker. Heat the solution to boiling, nearly

neutralize with ammonia and precipitate the sulphur with barium chloride.

It very seldom happens that all the hydrogen sulphide is not absorbed by the solution in the first funnel, so that generally it is only necessary to collect and dissolve the precipitate formed in the first funnel; should any form, however, in the second funnel, this must be collected and dissolved, and the solution added to that from the first funnel. The solution in the second funnel may be used over for many analyses.

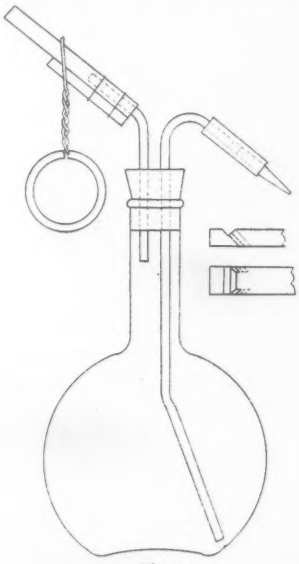
It is hardly necessary to caution chemists against allowing the solutions to stand for any great length of time, in the funnels, on account of their action upon the glass stop-cocks. The filters in the bottom of the funnels, if properly prepared, will last for many operations.

The apparatus may be used for the determination of sulphur by the method of absorption in cadmium chloride solution, with subsequent solution of the cadmium sulphide in hydrochloric acid and titration of the liberated hydrogen sulphide with iodine, or it may be used for determining sulphur by the Elliott method, or Drown's method of absorption in potassium permanganate solution. In either of the last two cases, the filters in the bottom of the funnels should be left out, since there is no need for them. The writer has found it much easier to wash out the funnels than U tubes and potash bulbs, thus saving time and trouble and lessening the chance of error.

Many other uses will suggest themselves to the reader, to which the apparatus, modified in one way or another, may be put.

Fig. 2 represents a wash-bottle which the writer has had in constant use for some time and found very convenient. Its construction is so simple and evident from the drawing, that a description seems almost unnecessary. It consists of an ordinary wash-bottle, fitted up as usual, except that the shorter tube is made of heavy-walled glass tubing. To this is fastened a piece of hard wood, three-eighths by one-quarter by one and three-quarter inches, notched with a V-shaped notch across its face and, with a groove cut down its either side, parallel to the neck of the flask. A sketch showing the piece of wood, in detail, is appended to the drawing. A piece of stout wire is bent

with a loop at either end. The larger of these loops is made of sufficient size to admit the thumb comfortably and is covered



Flg. 2.

with a piece of small rubber tubing to prevent chafing that member. The smaller is bent over the rubber tubing and wood and is large enough to slide up and down freely in the vertical grooves, with about half an inch play. The bottle is grasped by the last three fingers of the hand and the thumb is passed through the loop in the wire, leaving the first finger free to guide the jet. A slight pull from the thumb is sufficient to bring the wire down upon the rubber, pressing the latter into the notch and effectually closing the opening. By doing this, before ceasing to blow into the bottle, the fumes of the acid, or steam, or whatever volatile substance the bottle may contain, are prevented from passing back into the mouth or lungs and a steady stream is kept going from the jet for some moments, or until the pressure of the thumb is relaxed, without further effort on the part of the operator.

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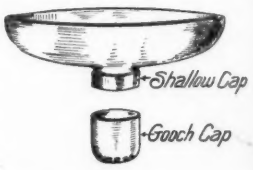
NOTES.

A Simple Fat Extractor.—To those making fat determinations in milk by means of solvents, the form of extractor represented in the accompanying cut will be found both convenient and accurate. It has been in use by myself and others for over three years, and in addition to being inexpensive and simple, it has been found capable of more rapid and fully as accurate work as many of the complicated and expensive forms of extractors. It consists of a small shallow dish spun out of very light copper, and fitted with two tight caps (see illustration). One is shallow while the other is longer, and perforated with several small holes on the bottom similar to a Gooch crucible. To use the extractor the shallow cap is fitted on the dish, as in the cut, then five cc. of milk are introduced and evaporated to dryness on a water-bath. I have found that one-half hour is usually sufficient to accomplish this, although, when porcelain milk dishes are used, three hours are considered necessary. The solids may now be weighed. The shallow cap is then removed, and placed inside the dish. The perforated cap having a thin layer of asbestos in the bottom, is put on, and the solids treated with the boiling solvent, ether or benzene. Care should be taken that the asbestos is so packed, that the solvent runs through slowly, say a drop every two or three seconds. The solution of the fat may be caught in a small beaker and the fat dried and weighed. I find that fifty cc. of the solvent is usually sufficient to remove all the fat, and although I have examined the residue many times for traces of fat, I have never succeeded in finding over one-tenth of one per cent. of the total fat present in the sample of milk. Were this dish made of platinum, instead of copper, besides being useful for various purposes in the laboratory, all the determinations called for in an ordinary milk analysis, for example, solids, fat and ash, could be made with a single sample, or five cc. of the milk under consideration.



VERNON J. HALL.

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The Exact Dilution of Liquid Reagents by Formula.—While a full set of hydrometers should be included in the equipment of every general laboratory, there may be, nevertheless, occasions when such instruments are not readily available. But even where no such lack of apparatus exists, there are a great many cases when, I believe, it is far easier and more convenient to accurately prepare solutions of any required specific gravities by the use of a simple, general formula, rather than by hydrometer.

Quite frequently the dilution of a reagent is attended by a considerable rise of temperature, which must either be reduced before a hydrometer reading can be taken or else the latter must be corrected, an operation necessitating not only the use of a thermometer but also more or less calculation. Then, too, there are many occasions when the quantity of solution required does not afford sufficient volume to permit the use of an ordinary hydrometer.

Suppose it be required to prepare a volume, V_t, of a solution whose specific gravity shall be S_2, by the dilution of a volume, V_x, of a reagent whose specific gravity is S_1. The problem is to ascertain the volume, V_x.

$V_t - V_x =$ amount of water necessary for dilution.

From the equation $V_x S_1 + V_t - V_x = V_t S_2$ it is found that $V_x = \frac{V_t(S_2 - 1)}{S_1 - 1}$.

Conversely, if it be required to dilute an exact volume of a liquid of certain specific gravity to one of different specific gravity, then by transposition: $V_t = \frac{V_x(S_1 - 1)}{S_2 - 1}$.

It is frequently required to dilute to a certain specific gravity with some reagent other than water. In this case, first consider water as the diluting agent, and find V_t as above. Then, if $S_3 =$ the specific gravity of the diluting reagent: $\frac{V_t + V_x}{S_3} =$ the volume of the same necessary to be added to volume V_x to give a liquid of the specific gravity required.

CHAS. D. HOWARD.

OBITUARY.

MR. THEODORE A. HAVEMEYER, for many years a life associate member of the American Chemical Society, died at his home in New York City, on April 26. He was born in that city in 1839, and practically his whole life was devoted to the industry of sugar refining, in which he came to take such a prominent position in this country. The facts of his successful career, which will be of interest to the members of the Society, are so well set forth in an article in the *New York Sun* of April 26th, that we cannot do better than reproduce it.

"Theodore A. Havemeyer was of the third generation of the Havemeyers, noted for their great sugar industry in this country. He was the son of Frederick C. Havemeyer, whose father, Frederick Charles Havemeyer, with his brother, William S. Havemeyer, started a refinery in Vanderveer street, this city, in 1800.

"Frederick C., the father of Theodore A. and Henry O. Havemeyer, retired from the business in 1835, but in 1858 went into the business again for his sons, purchasing an interest in the Williamsburg Husse warehouse property.

"From that beginning grew the business that to-day practically controls the sugar industry of this country, and has a marked influence on that of the world. Every year the large brick factory between South Third and South Fourth streets was improved, and the four sons, associating in business with their brother-in-law, established the firm of Havemeyer & Elder.

"The firm took a lead in the sugar refining business from the start. They had fifty men in their employ at first, and the business increased until before the recent consolidation of many refineries throughout the country by them the factory there employed nearly 4,000 men.

"Of the four brothers who started in the business, Henry O. Havemeyer now alone remains. George Havemeyer was killed at the refinery in 1862, and Thomas Havemeyer afterward retired from the business.

"In speaking of the causes of his success in business some years ago, Theodore Havemeyer said:

"'We were taught our business thoroughly. After leaving school I was sent to Europe to learn all I could concerning the business I was to follow for a livelihood. In 1857 I went to the Hamburg refineries, and thence, after quite a lengthy experience, I went to other cities of Germany, where I gained a knowledge of the most advanced methods of that day. On my return, in 1859, I went into my uncle's refinery in Vanderveer street, and from there I went into the business in Williamsburg. I made up my mind from the start that whatever was worth doing at all was

worth doing well. For twenty-five years I was at work at 7 A.M. and did not leave the refinery until 7 P. M. I never went to bed at night until I had gone through the whole establishment. Many times I worked all the night long. While I was a single man my expenses never exceeded $50 a month. Pilot bread and cheese made for me many a meal. A canvas suit was my daily apparel, and there was no part of the business at which I and my brothers did not work; no part we considered too dirty or too arduous or beneath us.

"'One prerequisite in any business is a thorough mastery of its principles and a knowledge of all its details. There was no part of the manufactory or no part of the refining business with which we were not thoroughly familiar. I knew how to fire up under the boilers, how to run the engines. I built an engine once myself. I knew how to refine the sugar and how to market it. I knew what was a fair day's work for a man, because I worked alongside of the men. Another requisite is application and alertness. We were always on the lookout for some better way to do a thing, and our success is largely owing to invention brought out by observation and experiment. Another need is integrity and promptness in business dealings. We always paid cash as we went along, but if one has to give notes they should be promptly met. We filled our orders always according to agreement. Another rule is to keep away from liquor, and we always followed it. The practice of these rules, combined with frugality and ordinary facilities of mind, will bring commercial success to any man.'

"The Havemeyers invented many labor-saving machines and methods, and by means of these and the immense capital employed, sugar, which was refined in their grandfather's time on a margin of 10 cents a pound, and in their father's time at 4 cents a pound, is to-day refined for 1 cent a pound.

"It was not alone in the sugar refining business that Theodore A. Havemeyer was prominent. His banking and real estate interests were enormous.

"Mr. Havemeyer was greatly interested in agriculture, and had one of the finest stock farms in the country at Rahway, N. J. Besides his handsome residence in this city, he had a magnificent summer home at Newport. He was interested in golf, and was really the father of golf in this country. He was President of the American Golf Association at the time of his death.

"For twenty-five years Mr. Havemeyer was the Austrian Consul-General in this city, having been appointed to succeed his father-in-law, Ritter von Loesy, in 1871. He resigned in 1895, and immediately there was much talk to the effect that he was to be ennobled by the Austrian Emperor.

"Mr. Havemeyer was 58 years old at the time of his death. He

was married 33 years ago to a daughter of Chevalier de Loesy, the then Austrian Consul-General here. He leaves a widow and nine children."

WM. MCMURTRIE.

BOOKS RECEIVED.

Variety Tests of Fruits. Tests of Vegetable Seeds. Bulletin No. 44. March, 1897. 48 pp. Agricultural Experiment Station of the University of Illinois, Urbana, Ill.

The Synchronograph. A New Method of Rapidly Transmitting Intelligence by the Alternating Current. By Albert C. Crehore and George O. Squier. Reprinted from Vol. 14 of the Transactions of American Institute of Electrical Engineers, N. Y. City. 31 pp.

Relations Between the Melting Points and the Latent Heats of Fusion of the Metals. By Joseph W. Richards. 5 pp. Reprinted from the Journal of the Franklin Institute, May, 1897.

Water and Public Health. The Relative Purity of Waters from Different Sources. By James H. Fuertes. x+75 pp. New York: John Wiley & Sons. Price, $1.50.

A Page from the Chemistry of To-day. By Charles A. Doremus, A.M., M.D., Ph.D. 23 pp. Press of J. J. O'Brien & Son, New York.

The Story of the Chemical Elements. By M. M. Pattison Muir, M. A. 189 pp. London: George Newnes, Ltd. Price, 50 Cents.

The Book of the Dairy. A Manual of the Science and Practice of Dairy Work. Translated from the German of W. Fleischmann, Ph. D., by C. M. Aikman and R. Patrick Wright. xxiv+344 pp. London: Blackie & Son; and New York: D. Van Nostrand Co. Price, $4.00.

Ninth Annual Report of the Storrs Agricultural Experiment Station, Storrs, Conn. 1896. 292 pp. Report of the Director; Bacteria in the Dairy; Study of Rations Fed to Milch Cows in Connecticut; Investigations on Metabolism in the Human Organism—Preliminary Account of Experiments on the Income and Outgo of the body and the Effects of Different Diets; Studies in Dietaries; Various Digestion Experiments; Average Composition of American Food Materials; Field Experiments with Fertilizers; Analyses of Fodders and Feeding Stuffs.

Proceedings of the Thirteenth Annual Convention of the Association of Official Agricultural Chemists held at Washington, D. C., November 6, 7, and 9, 1896. Edited by Harvey W. Wiley, Secretary of the Association. Bulletin No. 49, U. S. Department of Agriculture, Division of Chemistry. 1897. 127 pp. Washington: Government Printing Office.

ERRATA.

Page 390 (May number), line 9, for "bicarbonate" read "bichromate."

Page 414, Series 8, line 6, for "numbers" read "number."

Pages 420 and 421, at head of 3d column in tables, erase "Gms," (these numbers referring to cc. silver nitrate when amount of interferent is 0).

Page 427, Set III, second column, for "0.5" read "0.0."